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OILS, PIGMENTS, PAINTS, VARNISHES, ETC.

A CONCISE TREATISE ON THE MANUFACTURE, PROPERTIES, AND USES OF LIQUID PROTECTIVE AND DECORATIVE COATINGS AND THEIR INGREDIENTS

FOR STUDENTS AND ALL THOSE CONCERNED WITH THE MAKING OR APPLICATION OF THESE MATERIALS

BY

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PITMAN'S TECHNICAL PRIMERS

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PREFACE

Nearly all objects, large or small, which are made or used by man have upon their surfaces a coating composed of materials different from those of the objects themselves. The purpose of this almost universal condition is either protective or decorative; protective, because it is a fact that the materials best fitted for the formation of an article or structure are seldom the best suited to resist the external destructive influences of weather, abrasion, etc.; decorative for the reason that man has an aesthetic sense and it is of distinct value to him in his life to be surrounded by objects which do not offend this sensibility.

The aim of this volume is to deal tersely yet comprehensively with the manufacture and use of coatings of the type which are applied in liquid form and afterwards solidify. This subject clearly includes those coatings of which linseed oil is the basis, and as they are by far the most widely used type at present, they receive a treatment proportionate to their importance.

In general, the manufacture or origin of the materials used in the liquid compositions is dealt with briefly, but their properties and mode of use are described more fully, with

special reference to the technical points concerned in the manufacture of the coating and in the question of the values and deficiencies of the finished articles from the point of view of the user.

The matter herein is not merely elementary. By dealing with the subject from the point of view of first principles, so far as it allows, the writer has endeavoured to present it so that it will be understood by many to whom the details of the subject are fresh, and will yet be of value to the Works' Staff. A short bibliography is included to assist further study.

The numbers in the text refer to paragraphs in the book in which will be found other matter relevant to that under discussion.

The author is indebted to Messrs. Follows & Bate, Ltd. (Manchester), for the loan of blocks illustrating grinding and mixing machines.

RUPERT H. TRUELOVE.

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CHAPTER I

COATINGS FOR VARIOUS PURPOSES

THE nature of the coating for a surface varies widely according to (*a*) the nature of the surface to be coated, (*b*) the influences to which it is to be exposed, (*c*) the final appearance desired. Considerations (*a*) and (*b*) determine the nature and degree of *protection* to be provided, whilst (*c*) is of importance from the standpoint of *decoration*. Sometimes protection is subservient to appearance and sometimes appearance is of little account, but protection very important. As a general rule the need for protection need not prevent that for decoration being satisfied.

1. House Painting. For the decoration of those portions of buildings which lend themselves to this, oil paints and varnishes are almost exclusively used, both inside and out.

These consist of a "drying" oil, usually linseed oil (§ 7), with which a resin has been incorporated, to make a *varnish* (§ 12); or in which a pigment has been finely ground to make a *paint* (§ 26). Sometimes the paint contains a mixture of several oils, but linseed oil is nearly always the basis of the mixture; and sometimes the paint is made from a pigment ground in varnish of the type mentioned above. The ingredients and the proportions of them are altered according to the effect desired, and according to the position of the coat, whether inside or outside and whether a priming coat, one of the other undercoats, or the finishing coat. For instance, pigment is ground, not in oil proper, but in a suitable oil varnish, where high gloss and smooth surface are required, and such mixtures are known as *varnish-paints* or *enamels* (§ 30), of which a large number are on the market and are popular as the finishing coat, especially for interior decoration.

The interior walls of offices and dwelling houses, though very often papered, are frequently painted, and still more frequently distempered (§ 83). *Distemper* is a water paint, i.e. a water solution of glue or a similar substance in which pigment has been ground and possibly other materials introduced for specific purposes; e.g. to make the surface less soluble to allow of a second coat being applied without washing up the first, and to

allow of light sponging to remove dirty marks, and so on. For interior walls a flat or matt effect is desired, and distemper yields this well. If oil paint is used for walls it can be so compounded as to give a similar appearance. This is more lasting and hygienic allowing, as it does, of frequent washing without detriment, but it is much more costly than distemper both in itself and in application. With oil paint several coats are necessary, and these must be applied laboriously with a small brush, whereas distemper will often give a good effect in one coat, seldom more than two coats being necessary, and a very large brush and unskilled labour may be used.

For the *waterproofing* of interior walls to prevent dampness, a preparation of bitumen may be applied (§ 71), or a waterproof varnish such as a solution of manilla resin, etc., in an alcoholic solvent (§ 77). Such coatings should be applied at a period when the wall in question has become temporarily dry. A coating for the same purpose which could be applied to a wet wall consists of an emulsion of a drying oil or varnish in a glue solution. For use on the exterior of walls, preparations containing such materials as linseed oil, mineral oils, and water-repelling waxes are effective.

2. Floors. For the floors of buildings special paints are sometimes used, which dry

very hard and tough. These contain linseed oil or other drying oil, a considerable proportion of resin, and the pigment. The bare wooden floor showing outside the carpet in private houses is usually coated with a shellac varnish (§ 74), or a short-oil varnish (§ 66), which will stand much hard usage before wearing away. Alternatively, the boards may be coated periodically with a mixture of beeswax, linseed oil and a volatile thinner (turpentine) by rubbing-in.

Concrete floors which may dust and disintegrate when subjected to much abrasion can be protected from this by special paints which also improve the appearance of the surface, making it not unlike linoleum. Linoleum itself is oxidized linseed oil containing pigment, dried to a firm film in layer upon layer on a canvas base; resins, powdered cork, etc., are often incorporated.

3. Factories. In factories the whole question is usually one of protection and hygiene. Metal work in the buildings and structures is protected with oil paint (§ 26) or bituminous coatings (§ 71), but the inside walls are covered with a wash of lime (calcium hydrate) in water, applied roughly with a large whitewash brush or a spraying machine. This lime-wash, to which common salt is sometimes added, serves the double purpose of cleansing the walls and whitening the surface thus

lightening the interiors. The amount of light available in an interior is affected by the light-reflecting power of the walls to a far greater extent than is usually appreciated.* The lime in the course of a few days is principally converted to carbonate of lime which in this dry condition has great opacity and very high light-reflecting power.

4. Protection of Iron and Steel. One of the greatest problems before the engineer is to protect steel and iron structures from rust and consequent early destruction. The only method at present known is to coat the surface with a protective paint. For this purpose there are two types found effective, linseed oil paints (§ 26), similar to those used on the wood and stonework of dwellings, and black varnishes consisting of a solution of mineral bitumen, coal tar, pitch or similar material (§ 71). The latter admit of less skilful application and are much cheaper, but the former, if properly applied, protect the metal more certainly and effectively, besides allowing any coloured finish to be obtained. (*See* also §§ 55, 57.)

5. Furniture, Small Articles, etc. Small objects are coated to make them attractive,

* See also *Elements of Illuminating Engineering*, by A. P. Trotter, uniform with this volume. (Pitman, 2s. 6d. net.)

this being done with a great variety of materials of which perhaps shellac is the most important. Many wooden articles are French polished (§ 76), or coated with a spirit varnish to show up the grain, to enrich the effect, and to give a gloss to the surface. This treatment is that usually accorded to furniture. Small metal objects are usually coated with a hard drying pigmented enamel of oil and resin, or shellac basis which is baked on: or they are lacquered with a solution of shellac (§ 74), celluloid (§ 80), or oil and resin, after being polished, etched or bronzed, the coating being usually baked (stoved). Thus bicycles and similar goods are usually dipped into an enamel composed largely of linseed oil varnish and are then stoved to render the enamel non-tacky and hard.

Motor-cars, especially when the body is of metal, are often stoved after the application of a similar enamel. When the body is of wood and sometimes when it is of metal, and also in the case of horse-drawn vehicles, the painting is usually done by hand, a large number of coats being put on. Each coat is well rubbed down, and to facilitate this the undercoats are usually paints containing linseed oil, much resin, and also pigment (coach-builders' flatting paints, § 69). The last two or three coats consist of flatting varnishes covered by a first-class long-oil copal varnish (§ 20). Thus the very finest finish is obtained.

6. Submerged Surfaces. For the coating of surfaces of all kinds which are to be submerged under water, special compositions of a bituminous nature (§ 71) are much used, and are effective if several thick coats are applied, each being allowed to get thoroughly dry before putting on the next. These compositions are useful under salt water as well as under fresh. Salt water is far more destructive to iron and other metal work than is fresh water, owing to the fact that it sets up electrolytic action on the surface of the metals. This effect is of very serious importance in the case of ships, the steel hulls of which are relatively thin and are held together by rivets, the presence of which increases the likelihood of electrolytic action. The hulls of ships are painted with special compositions to protect the metal from the influence of sea-water, and a final coating is applied which contains poison to prevent the attachment of barnacles and seaweed to the ship's sides and bottom, which would otherwise be overgrown in the course of a few months, so that the ship's speed would be reduced considerably or the coal consumption much increased. Owing to the severity of the conditions vessels should be recoated every six months, and satisfactory results can only be obtained by the use of high-class materials and expensive poisons, scientifically manufactured into anti-corrosive and anti-fouling compositions.

CHAPTER II

LINSEED OIL AND DRYING-OIL VARNISHES

7. Linseed Oil: Raw and Refined. Linseed oil is a yellow-brown or greenish oil of rather low viscosity and characteristic smell, which is obtained from the seed of the flax plant. It consists of the glycerides of several unsaturated fatty acids, the mixed acids being termed "linoleic" acid.

Its use in the paint and varnish industry is due to its property of setting to a tough material, called "linoxyn," when a thin film of the oil is exposed to the air.

The analytical constants of raw linseed oil are: specific gravity, 0·930 to 0·935. Refractive index (25° C.), 1·479 to 1·484. Iodine value, 170 to 195. Saponification value, 190 to 195. The free fatty acid is very low in good oil, but may increase in old badly pressed oil, by the action of fat-splitting enzymes; it should not exceed 3 per cent (Acid value, 6).

These data apply only to ordinary raw linseed oil. Owing to the long time that raw oil takes to dry, and owing to its low viscosity, it is necessary to modify its nature to some extent before using it in paints and varnishes. The modifications are usually brought about by heating, blowing with air and adding small

quantities of certain compounds, which act as catalysts in increasing the rate of oxygen absorption and hence solidification of the film (§ 11).

Fresh raw oil contains a good deal of suspended and dissolved matter which is thrown out as jelly-like particles when the oil is heated. This action is known as "breaking." The material thrown out consists of albuminous matter, phosphates, etc., from the seed cells.

Oil may be refined in several ways. It may be kept for a long period, six to twelve months, while the injurious materials separate out and settle down, the clear oil from the upper layers being known as "tanked" oil. The settlement is called "foots," and is used for inferior purposes, such as making putty. Such oil is not called "refined oil" in the trade, the name "refined" being retained for pale oils which have been treated to remove their colouring matter, without the addition of "driers" (§ 8). One method is to agitate the oil with about 1 per cent of strong sulphuric acid, which coagulates and chars colouring matter and other impurities. On washing to remove the last traces of acid, a fairly light coloured oil is obtained with other properties not different from those of the raw oil. This is the usual method of refining, and is called acid-refining.

Linseed oil may be bleached by strong sunlight or "ultra violet" light, but this

method does not seem to be used much, if at all, at the present time.

If the oil is heated to about 500° F. for a time and allowed to cool it becomes much paler but also somewhat more viscous, though still quite thin. Such a process is used for some purposes, and is called heat-refining. In conjunction with a filtering operation, to remove the albuminous substances, etc., which break away from fresh oils so heated, the process of refining is completed to yield an oil against which nothing can be urged on the score of chemical contamination as may be in the case of acid-refined oil.

Many refiners have what they believe to be secret processes and are able to produce oils of remarkably little colour at a quite small charge above the cost of raw linseed oil.

8. Boiled Oil. Linseed oil to which a drier has been added during a heating process is known as "boiled" oil. Originally such oils were made by heating the raw oil up to as much as 500° F. and then adding salts or oxides of lead and manganese in quite small quantity (§ 11). It has been found, however, that a much lower temperature yields much paler oils and steam heating is now mostly used. At this lower temperature the viscosity of the oil does not increase and, in order to produce this desired change, air is blown through the oil.

When oils are very dark and quick-drying, i.e. containing much lead, etc., in solution they are termed "double boiled."

When oils are specially treated to give a very light-coloured boiled oil, lighter than raw linseed oil, they are termed "pale-boiled" oils. Such oils should not have much manganese incorporated, and are usually driered with a small quantity of a cobalt compound.

9. Stand Oil. When linseed oil is heated it becomes slowly more and more viscous (as measured at low temperature). This change is believed to be a simple polymerization of the molecules since the saponification value and acid value are but little altered even when a great change has taken place in physical properties. The drying capabilities are unaltered, and there does not appear to be any satisfactory evidence that the resulting oxidized film is other than the same linoxyn of raw oil. Such thickened oils are called "stand" oils.

This polymerizing action takes place the more rapidly the higher the temperature, the curve being similar to that of tung oil in character (Fig. 3, § 25). A temperature of 300° C. produces an oil as thick as golden syrup (and very like it in appearance) in about six hours. If the temperature is taken too high, secondary changes take place with the setting free of fatty acids, the giving off of excessive acrolein vapours (decomposition of glycerine) and

darkening of the oil. The same undesirable effects may be produced by careless manipulation even at lower temperatures owing to local overheating.

If linseed oil is heated in iron vessels the free fatty acid, small though it may be in quantity, nevertheless dissolves a little of the iron and the iron linoleate darkens the oil; so that where the palest heat-treated oils are required copper or aluminium vessels must be used.

10. Laboratory Work. In connection with this it is well to reflect that the greater the bulk of oil treated at one time the less the proportionate area of metal in contact with oil, and in the same way the less the proportionate area of surface exposed to air and to the fire's heat.

This remark bears very definitely on the question of reproducing in the works the results obtained in the laboratory. Table I shows clearly the difference between a laboratory pot and a large works pot as regards the proportions mentioned. In order to have, in a laboratory experiment in a 1-litre pot, the same conditions as exist in a large works pot, as regards metal surface and air surface, the 1-litre vessel should have a metallic surface of only 50 sq. cm. and a neck of only 10 sq. cm., instead of areas ten times as great. The laboratory pot can, and should be, constructed to fulfil these conditions.

TABLE I
COMPARISON BETWEEN LABORATORY POT AND LARGE WORKS POT

	Laboratory Pot. (1 litre.)	Large Works Pot. (approx. 1 ton.)
Volume of oil, cu. cm.	1000	1,000,000
Area of oil surface, sq.cm.	100	10,000
Surface of metal in contact with oil, sq. cm..	500	50,000
Ratio of air surface to oil volume . . .	0·1	0·01
Ratio of metal surface to oil volume . .	0·5	0·05

Similar discrepancies in conditions will be found on all sides, the more obvious being rate of heating and cooling. These and other factors are clearly the cause of the frequent failure to reproduce laboratory operations on a works scale, and thus these discrepancies should be recognized by the chemist and eliminated as far as possible by suitable expedients whenever the laboratory experiments are intended as forerunners of works operations.

11. Driers. Practically the only catalysts used to hasten the oxidation of drying oils are compounds of lead, manganese, and cobalt. The compounds which are active as driers are those which dissolve in the oil and become

part of it, such as the rosinates, linoleates and oleates (§ 68). The method by which these compounds are made, and introduced into the oil, or formed in the oil *in situ*, is immaterial

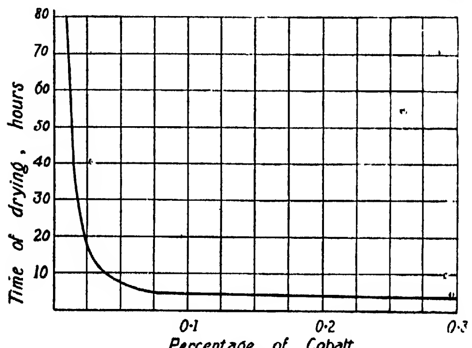


FIG. 1.—EFFECT OF A CATALYST (COBALT) ON THE DRYING OF LINSEED OIL, AT 60° F.

Note.—The time of drying is also affected by humidity, ventilation, and light.

as regards drying power; the quantities and proportions of the metals in solution being the governing factors.

Thus, cobalt oleate or linoleate may be made by precipitating sodium oleate or linoleate with a soluble cobalt salt, such as the chloride, in aqueous solution; cobalt rosinate may be made by dissolving cobalt hydrate or acetate in melted rosin at a high temperature; yet the time of drying of two oils to which

each of these driers have been added will be the same, providing that the percentage of metal actually in solution in the oils is the same in both cases.

In this matter of driers, dealing as we are with catalysts, we should expect them to follow the laws of catalytic action, as unravelled in other branches of chemistry. This they appear to do. The reaction is a time reaction, the rate of which increases with increase of temperature and with increase of concentration of the catalyst (Fig. 1); but the author knows of no quantitative investigations yet made to determine the exact physico-chemical facts. The subject is awkward owing to the difficulty of measuring the oxygen absorption, and still more owing to the imposition of other factors affecting the rate of oxidation, namely, the flow of air over the surface (a quick flow increases the rate of drying), the degree of moisture in the air, the absence or presence of light, and the thickness of the layer which can, of course, only react at its surface.

We find in this subject what appear to be examples of activation of catalysts (promotor actions), inasmuch as several of the metals which can cause the drying of linseed oil require the presence of much smaller quantities of other metals before they will function. In addition there is evidence that the metals only act as makers of the actual

catalytic agent, an organic peroxide body. Lead alone acts only feebly as a drier, but very small quantities of cobalt or manganese and certain other metals will greatly accelerate the reaction. Speaking always of molecularly equivalent quantities, manganese is almost as bad a drier when alone as is lead, but cobalt is a powerful drier when quite alone. Cerium can be activated by manganese in the same way as lead is activated, and it is similar in drying powers. Zinc, though often referred to as a "drier" does not exert any drying action in the same sense as do lead, manganese, and cobalt. Iron acts as a drier when in conjunction with manganese, though rather weakly. Most other metals have no drying powers.

Thus it is that we find the most commonly used drier to be not lead alone or manganese alone, but a lead-manganese combination; while cobalt is generally used alone.

The commonest drier is lead-manganese rosinate, the lead being much in excess of the manganese. This is made by adding litharge ($Pb\,O$) and pyrolusite ($Mn\,O_2$) to molten rosin and prolonging the heating till solution of the oxides is effected in the acid rosin, producing the rosinates which may then be dissolved in white spirit (§ 15) for convenience in adding to paint. This liquid is called terebine (§ 68).

The quantities of metal required to be in solution in oil to make it dry in a reasonable

time (8 hours at 15° C.) may be taken as in the neighbourhood of, lead 0·5 per cent, together with manganese 0·05 per cent; or cobalt alone 0·05 per cent.

12. Copal Varnish. *Definition.* The name "copal varnish" has long been known to cover that class of coating which dries partially by the evaporation of a volatile ingredient (turpentine, etc.) and partly by solidification of the remaining homogeneous film composed of an intimate blend of copal resin and linseed oil (§ 7).

Unfortunately the name has often been misapplied to other and inferior products in which there is no copal resin and in many of which rosin (§ 79) or rosinates preponderate. Such varnishes, while suitable for some purposes, which do not involve exposure to weather or abrasion, are usually rapidly disintegrated by the action of sun, rain and wind. Latterly, however, means have been discovered whereby varnishes, not containing any copal resin, may be manufactured which bear comparison with genuine copal varnishes in colour, rate of drying, lack of tackiness in the film, toughness of the film, resistance to rubbing, weather, moisture, etc., and in general appearance and durability; and which even surpass the genuine copal varnish in some of these qualities. This type of varnish is made from that hitherto undesirable substance rosin, with which Chinese

wood oil (tung oil) has been compounded (§ 24).

Ingredients. The ingredients of copal varnishes are linseed oil (§ 7), a volatile "thinner," and the copal resin itself. The volatile thinner may be turpentine or white spirit.

13. Turpentine. Turpentine is the product of the distillation of the resinous exudation ("oleo-resin") of a considerable variety of conifers (pines). The distillate is turpentine and the residue is the rosin or colophony of commerce (§ 79).

American turpentine has a specific gravity 0·860 to 0·875, is water white, and has a not unpleasant characteristic odour. It distils almost completely between the temperatures 150° to 170° C. The refractive index is 1·46 to 1·48. It is usually dextro-rotatory, while French turpentine is usually laevo-rotatory.

14. White Spirit. White spirit used in the paint trade is a product of the distillation of petroleum and is expected to conform, as closely as is consistent with its comparatively low price, with the volatility of turpentine; for turpentine has been found by long experience to have a rate of evaporation convenient for the application of coatings containing it. White spirit, owing to its nature and consisting as it does of a mixture of homologues of graduated boiling points, cannot have so

regular a rate of evaporation as turpentine. The usual figures expected of white spirit are as follows—

> Distillation points 145°C. to 210°C. with no oily residue.
>
> Flash point above 73°C. (to avoid coming under certain provisions of the Petroleum Act).

White spirits are also made which do not conform to this general specification, but in which special attributes are required. Amongst these are low volatility and high flash point; low volatility for use in flat-drying paints where the rate of evaporation shown by turpentine may sometimes be too great; high flash point for those paints in which a large proportion of the white spirit is used and which must conform to shipping companies' rules regarding inflammability.

15. Copals. The resins used in making oil varnishes are all called "copal" by courtesy, whatever may be their source, with some exceptions such as rosin (§ 79) and amber. This classing together of the oil varnish resins is justified as they do not differ from one another very much when made up into varnish, so little in fact that it requires expert knowledge to warrant an opinion even after careful tests have been made.

The original true copal is that from the East Coast of Africa called Zanzibar copal

or animi, and this is still the best of the copals, yielding the finest varnishes. Copals may be divided into two distinct classes: (1) those that are of recent origin, (2) those of prehistoric origin and called "fossil." The latter class is by far the harder and better for the purpose of making resistant varnishes. The copals are usually named after the country or port of shipment, and so it is easy to see how copal resins bearing the same name may yet be of different origin and nature. Thus from Manilla we have a hard resin used for oil-varnish making and a soft resin (§ 77) used for making spirit-varnishes, and there are grades of intermediate degrees of hardness.

Among the commercial copals there may be mentioned—

Zanzibar	East Africa
Sierra Leone	West Africa
Angola	West Africa
Congo	West Africa
Manilla	East Indies
Kauri	New Zealand

The areas from which these come mostly yield resins of both types, fossil and recent, the fossil being much harder, of higher melting point, and the more valuable type.

16. Varnish Plant. The varnish factory is so arranged that a series of pots can be heated over furnaces and quickly removed therefrom

at will. It is usual to have the furnaces below the floor so that the pot may rest in a hole over the furnace in such a manner that only a small portion (4 in. to 8 in.) of it is below the floor level, and consequently being fiercely

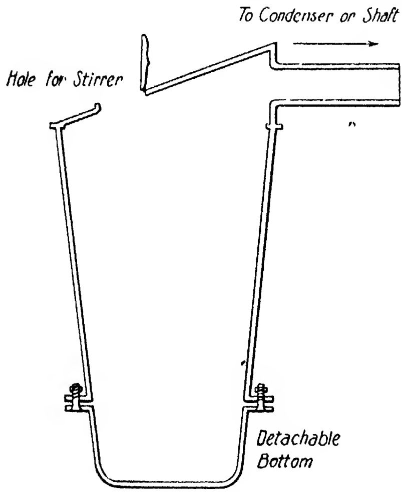


FIG. 2.—VARNISH POT.

heated. The pots used vary considerably in size in different works, but are always more or less of the type shown in Fig. 2. There is a hood leading to a shaft which carries away the fumes generated. The hood may be well

above the top of the pots or closely fitting, but in any case it allows of the free use of a hand stirrer. The pots are usually conical in shape, the upper portion being the wider, or are cylindrical, and have a flange at a suitable distance from the bottom which serves to support them when "sitting" over the fire. The bottom can be made detachable at the flange, to enable a new one to be fitted without returning the pot to the makers. From out the sides there may protrude studs or lugs by which the pots may be lifted with care and carried away on a hand carriage, or they may be permanently fitted to a truck. The particular design will depend on the quantity of gum to be melted at a time. This varies from a few pounds up to half a hundredweight or more; the tendency being to use larger pots which can now be done owing to the use of modern machinery, electric power, etc.

The pots are made of iron, copper, aluminium or of a suitable alloy. The use of iron tends to darken the varnish as the iron compounds, formed to a small extent, are very deep red-brown in colour. The traces of copper dissolved from copper pots are green, but are not in sufficient quantity to influence materially the colour of the resins. Aluminium has the advantage that its compounds are entirely free from colour; also, the metal is a good conductor of heat and this, in a thick pot, helps to prevent local overheating and

consequent charring. The disadvantages of aluminium are its low melting point and its softness.

The furnaces are fed from either inside or outside the building, and are often gas-heated. Provision is made for accidental ignition, and should a pot catch fire it is immediately wheeled outside and a hood placed over it to smother the flames.

The pots are always very big in proportion to the quantity of resin melted in them because there is much frothing during the process. The pot must always be filled with gum above the level of the floor, otherwise the heat of the fire acting at the surface of the gum might fire it.

17. Melting Resin in Varnish-Making. The melting of the resin is known as "gum running." The correct quantity of resin, in pieces not too large (up to the size of walnuts), is placed in a pot and put over a fire as described (the stirrer being worked about a little now and again). This stirring becomes easier as the resin melts and finally the resin can be stirred as easily as oil and will run off the stirrer as a limpid liquid. During the melting much fume is given off, which amounts to from 5 per cent to 30 per cent by weight of the resin, and may be condensed and used in certain types of paint (§ 64). The quantity depends on the particular resin under treatment, on the degree

to which it is desired destructively to distil the resin, and to some extent on the skill of the manipulator.

The proportion usually distilled away of the different resins before they become fit for amalgamation with oil is roughly as follows—

Zanzibar . .	15–20%
Sierra Leone .	10–15%
Angola . .	20–25%
Congo . .	25–30%
Manilla . .	25–30%
Kauri . . .	15–20%

This loss must be taken into consideration when calculating the proportion of oil desired in the finished product. The amount of loss will vary with each delivery of resin and the exact loss to be expected can only be gauged by a trial run under working conditions. Tests on a small scale in the laboratory may be misleading, since the loss will depend to a considerable extent on the time taken, temperature of walls of pot, rate at which fumes are carried away, final temperature, etc. (§ 10).

When the resin is melted to the correct degree, which is usually taken as being that condition when the liquid will run freely off the stirrer and contains no lumps of unmelted resin, the oil is introduced little by little (§ 19) in such proportions that the mass is not chilled sufficiently to cause a separation of the resin and added oil. To assist this, the oil is added hot, it having been got ready in

another pot. It will assist the varnish maker to make use of thermometers in the oil and in the resin mixture, and to keep a record of these temperatures as the process proceeds for future reference and to assist him in tracing the cause should any batch turn out different from expectation in any particular. The use of thermometers is especially necessary when dealing with Chinese wood oil (§ 25) or any mixture containing it.

18. Preparation of Oil in Varnish-making. Only the best tanked or heat-refined oils (§ 7) should be used for varnish-making, any inferior batches of oil being kept for making boiled oil or for use in the rougher types of paints.

It is necessary to specify tanked oil as it is essential to the production of good varnishes that the oil should not "break," i.e. throw albuminous and other materials out of solution when heated.

While the resin is being prepared, the oil in the quantity required for the run is heated up to a convenient temperature for its addition to the resin, say, 150° to 200° C., and that may be all; or the oil may be "bodied up" considerably, approaching stand oil (§ 9) in consistency, by heating for a considerable period, say three or four hours or more, at 300° C. The latter type of oil requires more care to be taken in adding it to the melted

resin as it is more likely to refuse to mix and spoil the batch by charring and solidification.

Sometimes Chinese wood oil is used in conjunction with linseed oil for oiling-up the resin, and when this is used extreme care has to be taken to avoid solidification, which will occur in this case even after the oil has been satisfactorily combined with the resin. It may happen with very little warning, the whole mass going solid and being then practically unusable for any purpose. This danger is increased by an increase in the proportion of the wood oil, and it is very difficult to avoid disaster when the proportion of wood oil exceeds 50 per cent of the oil.

19. Oiling-up Resin. If the oil is added in too great a quantity at a time, some of it will not immediately dissolve in the resin and a mixture of resin-oil and oil results, and the necessarily high temperature of the process being too high for the uncombined oil, polymerization and solidification may occur before complete amalgamation is effected. The whole batch is then spoiled. To avoid this risk, the oil is added in small quantities at a time so that the whole of the addition is immediately dissolved by the resin. That this has occurred each time can be seen by noting if the fused mass is still limpid and clear. If now a spot of the mixture be dropped on to a piece of glass it will be seen to be clear, but it will

become cloudy as it cools; this cloudiness is due to the resin and oil separating again at the lower temperature. The mass in the pot is now maintained at the heat found most suitable by previous experience until a drop upon glass no longer becomes cloudy on getting cold. It is then time for a further addition of oil in the same way as before. The mass is heated and tested for amalgamation as after the first addition before a third addition is made, and so on until all the oil has been added and the last addition tested for complete combination, when a drop of the varnish should still remain perfectly clear.

It will be seen from the foregoing description of the oiling-up of a resin that the combination is not merely a physical mixing or solution but that a chemical reaction takes place between the resin and the oil which takes a definite time, decreasing with temperature, for its fulfilment as do most organic reactions (the so-called "time reactions").

A rough and ready method of oiling-up in small batches is to allow the resin to froth up in the pot after melting, add one-third of the oil which, cooling the mass, causes the froth to break and settle down, then continue the fierce heating till frothing again occurs, add one-third more oil to destroy the froth and repeat so that all the oil has been added. Finally, a test is made for the completion of the reaction as above.

20. Thinning Varnish. After the oiling-up process, the varnish is finished off by wheeling the pot away from the fire and out into the open where turpentine or white spirit or other volatile thinner is added as soon as the temperature has fallen low enough to make this proceeding possible (but see also § 21). The temperature of the varnish mass should be as low as practicable to avoid loss of volatile spirit by boiling or evaporation. In long-oil varnishes, that is those containing a high proportion of oil (from 70 per cent upwards), the thinning may be done at quite a low temperature as such a mixture of oil and resin can easily be stirred until it is quite cool, but with a short-oil varnish (§ 66), that is one in which there is only from 30 per cent to 50 per cent of oil, the volatile thinner has to be put in while the resinous mixture may even be above the boiling point of the volatile matter, and hence frothing and loss occurs during its addition.

21. Set-Pot Process. The varnish is often put through an additional process before thinning out, namely, heating in a large "set" pot at a high temperature for some hours, up to six hours, in order to thicken the varnish mass (or the oil it contains) much in the same way as stand oil is made (§ 9).

A set pot is a large pot built in by brickwork and fitted with a hood to carry away the

fumes. It may be fitted with power stirrers and is usually made of steel or iron. This does not darken the oils so much as when used in the smaller pots because the ratio of iron surface attacked to volume of varnish is much lower (§ 10); also, the temperatures encountered are lower although the time of exposure to the surface is greater. Another purpose of the set pot treatment is to make one uniform whole of a number of separate varnish runs. The set pot contains many separate runs, and so the heating in it may vary from half-an-hour to three hours according to the purpose of the treatment.

22. Adding Driers to Varnish. Varnishes made as above would take too long to dry unless a "drier" (§ 11) were added at some time during the process. Driers may be incorporated in several ways—

(*a*) By treating the oil with litharge and manganese borate, oxalate or similar compounds, when heating it before adding it to the fused resin. This method is not to be recommended because only dark varnishes could thus be obtained, and no satisfactory argument can be suggested in its favour.

(*b*) By addition of litharge and a suitable manganese salt, or manganese dioxide to the hot mass after oiling-up is completed. This also will tend to darken the varnish, especially if the black oxide of manganese is used.

(*c*) By addition of rosinates or linoleates of lead and manganese, after the oiling-up process. This is the more usual method.

(*d*) By addition of liquid drier or terebine (§ 68) to the varnish during the thinning process with the volatile spirit. This method is to be recommended as interfering least with the colour of the varnish, and is the least likely to complicate the manufacture by causing skins to form and premature oxidation to occur as may happen when one of the other methods is adopted.

(*e*) By "churning" the completed and cooled varnish in a simple horizontal mixer with the requisite litharge, etc., in which case dried zinc sulphate or ferrous sulphate is generally added as well. Such churned varnishes are usually very pale and clear, but tend to be slow drying.

23. Tanking Varnishes. The last treatment to which varnishes are put is one of clarification, for which the best method is to allow them to remain in large tanks at a uniform temperature for a very long period, up to a year or more.

The traces of undissolved resin, inorganic matter, excess driers, and gelatinous flocs from the oil gradually settle down leaving the varnish clear and in such a condition that it can yield a perfect, full-gloss surface unmarred by any irregularities. A quicker method

which is used for cheaper grades of varnish and has come into more favour in recent years is to pass the varnish through a centrifuge or filter-press,* either whilst it is still warm, or after standing some little time to cool and allow the impurities which would be thrown out on cooling to be removed.

24. Wood Oil Varnishes. As has been previously mentioned there have been made in recent years quite excellent varnishes, suitable for use in the place of "copal" varnishes but not containing any "copal." This result has been attained by the use of Chinese wood oil or tung oil (§ 25) in conjunction with common rosin (§ 79).

These varnishes are remarkable for the way in which their oxidized films appear to resist the absorption of water, for they do not become milky when exposed to rain or mist ("blooming") as do nearly all other types of varnish containing much oil. They may be made very elastic by including a large proportion of linseed oil in the recipe, and may even then be very tough. They grow progressively harder and tougher as time passes to a much greater extent than do the true copal varnishes, and by the shrinkage of the film they tend to yield large open cracks

* For information on these machines and other filtration processes, see *Filtration*, by Roland Wollaston, uniform with this volume. (Pitman, 2s. 6d. net.)

after long exposure, whereas copal varnishes though cracking earlier show small cracks which do not open. They resist abrasion and scratching very well.

25. Tung Oil. Chinese wood oil or tung oil is a rather viscous, light-coloured oil of

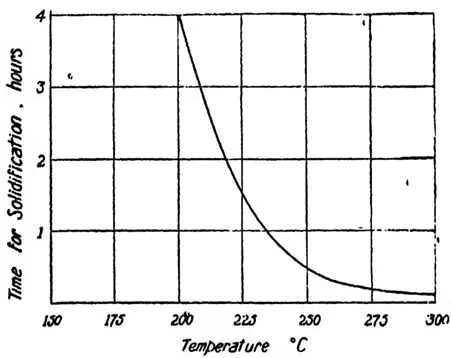


FIG. 3.—POLYMERIZATION CURVE FOR TUNG OIL.

Note.—At 160° C. the time for solidification is 25 hours.

characteristic unpleasant odour. It dries more rapidly than linseed oil when spread in a thin layer and exposed to air but, unlike linseed oil, its dry film is opaque, waxy and wrinkled. When suitably treated (driered), however, the film can be glossy, clear, hard and tough. Another characteristic property

s that of thickening and finally gelatinizing to a firm almost dry mass when heated above 250° C. for a few minutes. The rate of polymerization varies with temperature, *see* Fig. 3. The presence of fatty acids, rosin, or lime will delay this polymerizing action, which is used as a test of purity.

The physical characteristics of tung oil are—Sp. Gr., 0·940 to 0·943. Refractive index, 1·52. Iodine value, 165. Saponification value, 190 to 195.

CHAPTER III

DRYING-OIL PAINTS

26. Typical Recipe. For this discussion of paint it will be convenient to take a good all-round recipe, show how it is evolved, and explain the functions of the several ingredients. Such a recipe is—

	Per cent by Weight
Boiled Linseed Oil (§ 8) . . .	30
Zinc Oxide (§ 37)	20
White Lead (§ 40) (Basic Carbonate) .	20
Barytes (§ 43)	20
Coloured Pigment	5
White Spirit (§ 14)	4
Drier (§ 68)	1

It has been the custom in the building and decorating trade to refer to stiff pastes of pigments in oil as "paint," but in this work the word "paint" always refers to the coating material as prepared for use.

27. Oil for Paints. The oil is the basis of the mixture and gives it its cohesion after application and completion of the setting process with the formation of the solid film ("linoxyn"). It is also the principal agent in resisting the destructive agencies. Oil

alone, however, does not give adequate protection or good appearance because it is so thin that—

(1) It soaks in to many surfaces.

(2) It recedes from raised portions of an unsmooth surface, leaving these portions practically unprotected, and runs down in drops, leaving some areas very thinly covered.

(3) It dries soft and somewhat tacky. These defects are corrected in the admixture called "paint."

The soaking-in is allowed for by giving two or more coats, but it should be realized that this property is desirable in the first coat to enable this coat to get a firm hold on the surface—the oil flowing into the material and drying therein in union with that oil which remains in the solid powder ingredients of the paint.

The tendency to drain away from raised portions of the surface is overcome by the presence of the solids which, giving a slight pastiness, reduce the capacity for flowing, hold the oil on the raised portions of the surface by capillarity, and in the same way prevent the oil from flowing down in drops (§ 28). Of course, there are infinite gradations between pure oil which can only remain in a very thin layer on a vertical surface (the thickness of the layer depending principally on the viscosity of the oil) and a thick pasty paint which will stay on a surface as thickly as one

cares to place it there. A desirable consistency for a normal type of paint is that which will not allow the paint to run down a vertical surface, unless applied more thickly than will yield a film which will set right through (§ 31) in the course of a reasonable period, say, twenty-four hours. At the same time the actual medium must be of low enough viscosity to enable the brush to work it freely over the surface.

The third defect of pure oil—that of drying soft and tacky—is rendered less evident by the pigment which now enters into the composition of the surface of the paint, lessening the effective area of "dried" oil which is the sticky portion and also probably functioning by partially absorbing the still liquid portions of the oxidized oil film which are the cause of this stickiness.

Moreover, another factor is introduced in consideration of paint, inasmuch as some of the solid powders added enter into an actual chemical union with the medium, causing in some cases an increase in the consistency and, what is more important, causing a change in the chemical and physical nature of the final oxidized product.

28. Mixed Pigments. This brings us to the chief reason for the introduction of two opaque white ingredients in our specimen recipe (§ 26). Linseed oil when ground with

basic carbonate of lead gradually combines with it to some extent and the film from such a paint after being dry a long time, has quite different properties from those found when zinc oxide is used instead of lead carbonate. The lead paint film is softer, and the zinc harder but more brittle, while the lead wears away under atmospheric influences more easily than the zinc. The use of a mixture of the two pigments modifies the defects of each to give a result which is better than that obtained when either is used separately. It seems probable that, in the change from oil to linoxyn, active constituents of the pigments enter into combination with the linoxyn, considerably modifying the properties of the final product. Thus when zinc and lead active compounds (zinc oxide and basic lead carbonate or basic lead sulphate, § 41) are both present, the product is partly the zinc compound with its own capabilities and partly the lead compound with its own special characteristics.

Barytes, although practically transparent in oil, is usually introduced into the specification of a paint as it is a cheap article, and so lowers the cost "per cwt." (§ 62), but it must not be thought that this is its only recommendation. It functions satisfactorily as a solid powder, producing the specific qualities of paint as distinct from those of varnish, as already described. The particles of barytes will lie closely together, thus yielding a denser

mixture than can be obtained with other fillers, and this property is believed to be advantageous in a paint, increasing its durability (analogously with cement); and also permits a thicker layer to be obtained in one coat (§ 31).

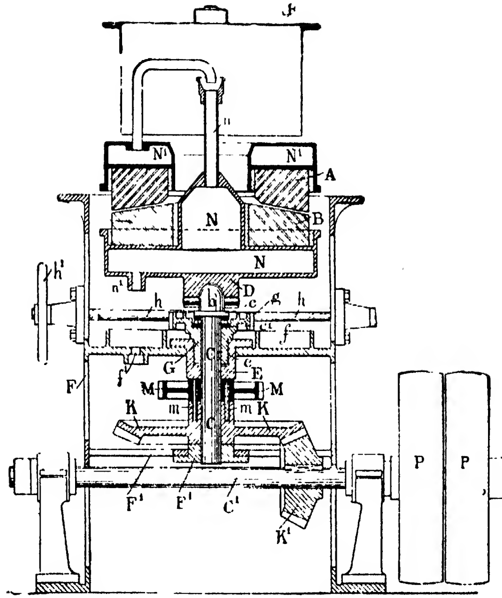
The coloured pigment is not introduced solely on the score of colour, since tinted paints have been proved more durable than white. If white were required, the coloured pigment would be replaced by more of the white pigments. The turpentine or white spirit is put in to assist in application—it reduces the viscosity of the medium, thus allowing freer working under the brush. It evaporates quickly, and enables the paint to set (become more pasty) before separation into layers (according to specific gravity of pigments, etc.) or exposure of raised points of the coated surface can take place to any great extent.

29. Percentage and Kind of Oil. To refer again to the most important portion of the specification, namely, the oil, 30 per cent of oil gives a good paint with good gloss and maximum protective power, but a considerably lower percentage could be used. If the percentage of oil be increased, the paint tends in proportion to become too fluid and to show the defects of the oil alone (§ 27). The oil here specified is boiled linseed oil, but

if the paint is to be used as a first coat on a porous or perished surface it is advantageous partially or wholly to substitute this boiled oil with raw linseed oil (to which the necessary extra drier has been added) because of its greater penetrating power, due in part to lower viscosity. Recent American official specifications frequently indicate raw or refined linseed oil (adequately driered) instead of boiled oil, which, in England especially, is more usual. If the surface to be painted is very absorbent the proportion of oil should be increased to allow for this.

30. Enamels. If a very high gloss is required for the finishing coat, for the sake of its appearance, or to have a surface which would be as little as possible likely to harbour dust, bacteria, etc.; then the introduction of copal varnish and the reduction of the proportion of pigment will achieve this, for reasons which are obvious—this approaches the nature of an "enamel," which is nothing but a very finely ground paint (§ 34), usually of very high gloss.

White enamels are largely used for interior woodwork, and will last for very long periods. They will stand frequent washing without detriment to the surface and after many years their appearance may be better than when fresh, if carefully treated. Enamels are not used very much for exteriors, but here they



A = Upper stone.
B = Lower stone.
b = Spindle head.
CC^1 — Centre spindle and driving shaft.
cc^1 — Collar of spindle, and ball race.
D — Water jacket.
E = Fixed casting.
e = Threaded surface.
E^1 = Bearing.
FF^1 = Frame.
ff^1 — Open water tray and water outlet.
G = Bearing adjustable for rise and fall.
hh^1 = Adjusting shaft and wheel.
KK^1 = Bevel gear.
M = Cog wheel driving stirrer in mixer at top.
NN^1 = Water spaces.
n = Water pipe.
n^1 = Water outlet to tray *f*.
PP = Fast and loose pulleys.

FIG. 4.—WATER-COOLED FLAT-STONE MILL FOR ENAMEL AND OTHER VERY FINE GRINDING.

would be found to give excellent service as finishing coats.

These remarks apply only to enamels which are made properly and from the best materials. The suitable materials are long-oil copal varnishes (§ 20) and "stand" oil (§ 9) as the binding media, and, in the case of whites and tints, zinc oxide as pure as possible as the white pigment. In order that the correct enamel-like surface may be obtained, enamels are made rather viscous and considerable skill is required to get a good even layer upon the surface, without allowing brush-marks or runs to show.*

The details of the specifications and manufacture of the many proprietary white enamels are guarded secrets, but it may be taken that—

(1) Zinc oxide of the best possible colour and purity is used.

(2) The medium does not "feed" (i.e. combine chemically) with zinc, or does so only to a small extent.

(3) The medium is thick and an excess is used.

(4) The drier is a pale one, usually with cobalt as the active principle (*cp.* pale boiled oil, §8).

(5) The grinding of the zinc oxide is done very finely indeed (§34).

31. Thickness of Oil-Paint Film. The thickness of an ordinary driered linseed oil film which will dry solid right through in a

* Practical hints on painting, enamelling, etc., are given in *House Decorations and Repairs*, by Wm. Prebble, uniform with this volume. (Pitman, 2s. 6d. net.)

reasonable time is about 0·03 mm. If oil in a layer appreciably thicker than this is exposed to air, a skin of approximately this thickness forms, leaving a still fluid layer between the solid film and the underlying surface, which remains fluid for a very long time. The amount of linseed oil dried by unit surface exposed to air is a more or less fixed quantity. Now, if the oil is mixed with pigment in the form of paint the amount of oil dried (oxidized) per unit surface remains about the same, but owing to the presence of the solid pigment particles, this represents a thicker layer, consequently the greater the proportion of pigment present *by volume*, the thicker the layer of paint which will dry to a solid film right through.

As the thickness of a simple oil film formed is about 0·03 mm., and that of a paint, say, 0·05 mm., it will be desirable to make the paint of such a consistency that it will ordinarily spread in a layer thinner than this, to allow for the inevitable unevenness of a surface and of a man's work, causing thicker layers in some parts than in others. This covering capacity of the paint will represent about 50 sq. ft. per lb. or about 600 sq. yd. per cwt. for a paint of specific gravity 2·0, weighing 20 lb. per gallon.

The above remarks are intended only as rough guides to an understanding of the subject, for many other factors enter into

the matter. For instance, the presence of certain substances will increase the thickness of the layer of oil that will dry through on exposure to air. Zinc oxide has this effect, as is seen notably in enamels (§ 30), possibly by combining ("feeding") with acid substances formed during the oxidation of the oil before the formation of the firm linoxyn itself. Chinese wood oil (§ 25) causes, under certain conditions, the formation of quite a thick solid skin, indeed some mixtures made up into varnish will show a gelatinous skin up to an inch in thickness in the package.

32. Specifications for Oil Paints. In the compounding of paints it is extremely important as well as a useful guide to remember that pigments vary greatly in the amount of oil required to make a stiff paste with them, and that the volume of oil required to make a practical paint of similar working ease will in each case be the same proportion of the paste, *by volume*, say, about one-half. Thus a pigment which requires more oil than another to make a stiff paste requires even more, in proportion, to make a workable paint. This is the root of the generally believed inferiority of zinc oxide compared with white lead as an obliterating agent when made up into paint, in spite of the much greater opacity of zinc oxide pigment, weight for weight (§ 33).

As a useful guide, the following may be

taken as satisfactory specifications for paint, and are mostly based upon British official requirements. In each case the drier is specified to be added in such quantity that the paint dries in from 10 to 15 hours at 15° C. The paint must dry to a semi-glossy film.

TABLE II

TYPICAL SPECIFICATIONS FOR OIL PAINTS

Pigment.	Percentages, by weight.		
	Pigment.	Oil.	White Spirit.
Basic Carbonate White Lead (§ 40)	84	12	4
Zinc Oxide (§ 37)	72	23	5
Lithopone (§ 39)	76	20	4
Black Oxide of Iron (§ 52) . .	70	26	4
Red Oxide of Iron (§ 52) . . .	64	31	5
Yellow Oxide of Iron (Ochre) (§ 54)	58	36	6
Mid Yellow Chrome, Orange Chrome, Lemon Chrome (§ 56) . .	65	29	6
Light Brunswick Greens, Dark Brunswick Greens (Containing 90% barytes) (§ 60)	78	19	3
Umber, raw or burnt (§ 53) . .	50	45	5
Lithol Red Lake (§ 62) on blanc fixe (§ 44)	80	17	3

33. Importance of Volumetric Composition. Since the ingredients are all bought by weight and most paints are sold by weight, this has

led to an unfortunate mental attitude, in regard to the qualities of the various ingredients, in which a weight basis is taken for comparison whereas a volume basis would be the more correct one. Thus, in comparing one pigment with another with regard to its behaviour in paint the proportion of pigment to oil *by volume* should be considered and not the proportion *by weight*, as is so often quoted ; to do this, one must determine the specific gravity of the particles, and the whole matter should be thoroughly examined (*see* Table III).

TABLE III

PHYSICAL CHARACTERISTICS OF TYPICAL PIGMENTS

PIGMENT SUBSTANCE.	Absolute Specific Gravity of Particles.	Absolute Specific Volume of Particles.*	Volume of unit weight dry Powder.	Oil required to make 100 pts.(by w'ght) into Paste.
	Water = 1·0	Cu. cm. per grm.	Cu. cm. per grm.	Parts, by weight.
Barytes . . .	4·3	0·23	0·42	9
China Clay . .	2·4	0·42	1·2	50
Oxide of Iron (Turkey Red)	5·0	0·20	0·77	25
White Lead .	6·5	0·15	0·42	8
Zinc Oxide . .	5·3	0·19	1·1	16
Ochre . . .	3·5	0·29	0·96	30
Red Lead . .	9·0	0·11	0·30	9

* Assuming no interstices.

The ability to spread under the brush with a given quantity of oil appears to decrease with increasing oil absorption (i.e. the quantity of oil required to make the pigment into a

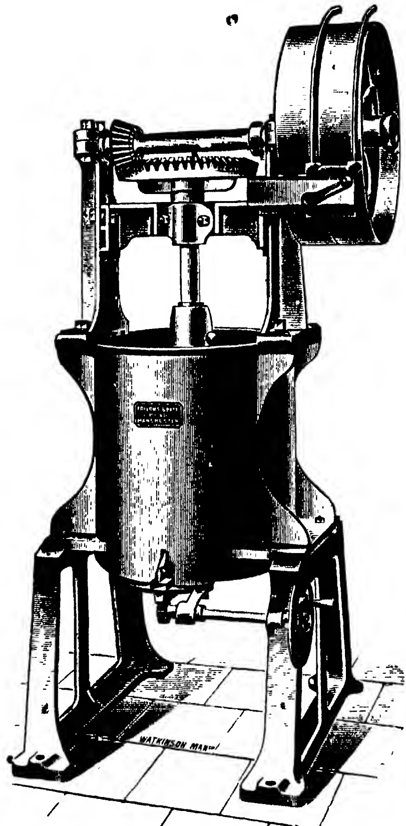


Fig. 5.—Vertical Pug Mill for Mixing Stiff Pastes.

stiff paste), while the ability to level or flow out appears to bear a relation to the volume occupied by unit weight of dry powder pigment,

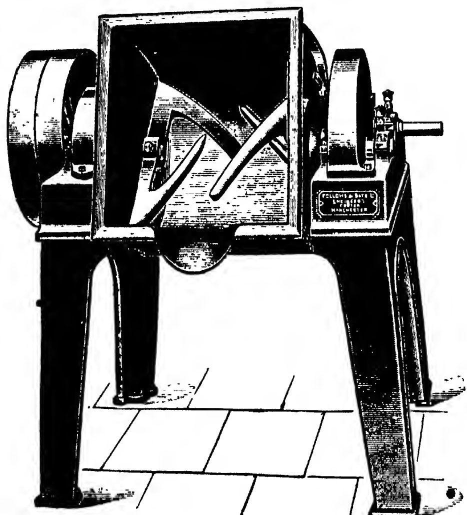


FIG. 6.—HORIZONTAL PUG MILL FOR MIXING STIFF PASTES.
Shown tipped for emptying.

the denser powders making more easily levelling paints. The paint chemist should be familiar with these physical properties of the various pigments he uses; their bearing on the costing question, both in regard to cost per cwt.

and cost per gallon, especially under fluctuating market conditions; and their bearing on the

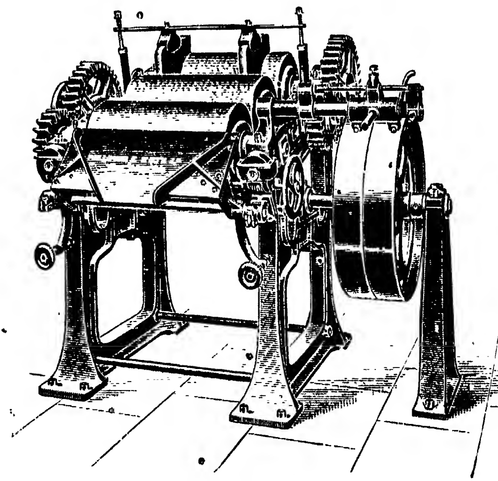


FIG. 7.—TRIPLE-ROLLER MILL WITH GRANITE ROLLERS, FOR GRINDING STIFF PASTES.

(*See* also Fig. 8.)

working qualities, flow, opacity, gloss, and durability of the paints made from them.

34. Manufacture of Oil Paints. The process of paint-making is simple; the oil medium is incorporated with the pigments by grinding. First a thick paste is made by mixing oil and

pigment in a pug mill (Figs. 5 and 6, pp. 46, 47) and passing the mixture between granite rollers revolving at different speeds, as shown in Figs. 7 and 8, pp. 48, 49.

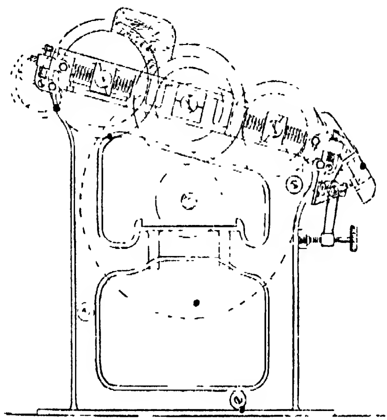


FIG. 8.—END ELEVATION OF TRIPLE-ROLLER MILL AS IN FIG. 7.

Showing springs holding rollers, and one method of gearing to obtain different speeds of rollers. The gearing illustrated gives roller speeds in the ratio 1 : 2 : 4.

The rollers may be 2 ft. or 3 ft. in length, and the centre one may have also a lateral motion. After grinding in the rollers the paste is thinned out in a horizontal or vertical cylinder fitted with stirrers (Figs. 9 and 10, p. 50); or,

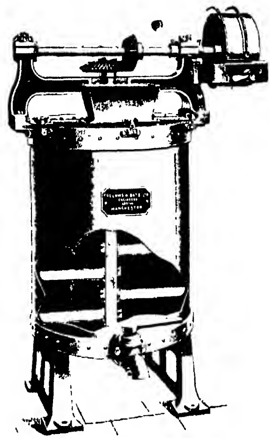


Fig. 9.—Vertical Mixer for Final Thinning and Amalgamation of Paint.

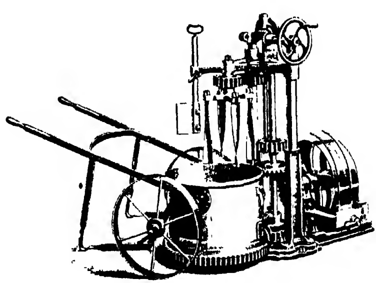


Fig. 10.—Mixer for Finishing Paint.

in small quantities, the paste is stirred by hand with the added extra medium (say, oil, turpentine, and terebine).

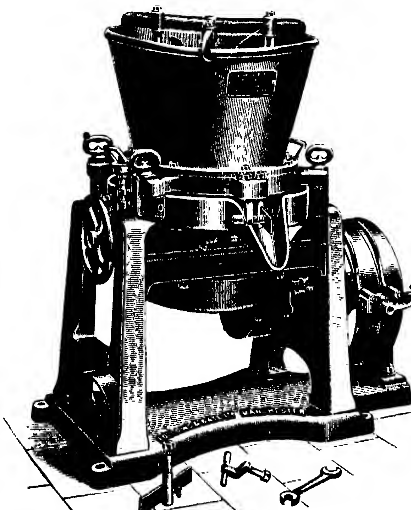


FIG. 11.—CONE MILL FOR GRINDING THIN PASTE AND READY-MIXED PAINT.
(*See* also Fig. 12.)

A still simpler process is that in which the ingredients are mixed into a thin paste in suitable simple mixers, ground through cone mills (Figs. 11 and 12, pp. 51, 52), and thinned

out to completion in a second simple mixer (Fig. 9, p. 50).

For very fine grinding of "enamels" special

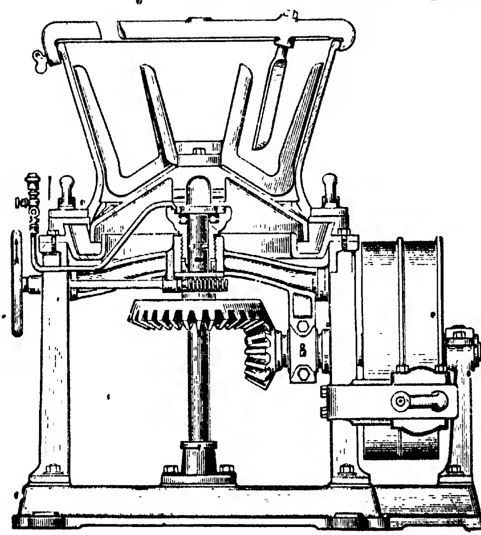


FIG. 12.—SECTIONAL VIEW OF "UNIVERSAL" CONE MILL (AS IN FIG. 11).

flat-stone mills, fitted with water cooling, may be employed (Fig. 4, p. 40), or the pigment may be ground very carefully in good roller mills with a thin oil and afterwards mixed with the special more viscous varnish medium required to complete the enamel recipe.

CHAPTER IV

PIGMENTS AND SOLID FILLERS

35. General Requirements. Any material which can be obtained in a sufficiently fine state of division—that is, of a size such that the largest particles are smaller in their largest dimension than the thickness of the paint coating (§ 31) in which they are to be used—could be employed as a pigment, subject to the following provisos in addition. It must not be sufficiently soluble in the medium or react with it to modify the properties of the mixture, to too great an extent. For nearly all purposes other properties are necessary, such as insolubility in water, non-volatility, and a certain degree of permanence when exposed to light, oxygen, carbon dioxide, etc.

The commonly employed pigments all conform more or less to these obvious necessities but vary appreciably in this respect. For example, zinc oxide (§ 37) and basic lead carbonate (§ 40) will react to some extent with oil media, especially when resins are present, modifying the nature of the liquid paint sometimes in a way and to a degree which is considered desirable (§ 31), but sometimes to such a degree as to render the paint, after the lapse of time, unsuitable for application to a

surface. Whiting (§ 48) (calcium carbonate) will react in a similar manner and is poor in its resistance to atmospheric influences; also,

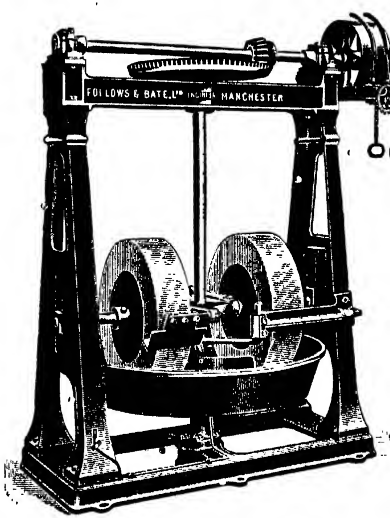


FIG. 13.—EDGE-RUNNING MILL, ROTATING PAN TYPE.

For grinding dry colour, etc.

it will dissolve in water which contains carbon dioxide. Barium sulphate (§ 43) is practically insoluble in water, and is uninfluenced by any ordinary conditions, but calcium sulphate (*terra alba*, § 49), is appreciably soluble in

water and commercial barium sulphate sometimes contains this. These differences, advantages and deficiencies are discussed further under the headings of the separate pigments.

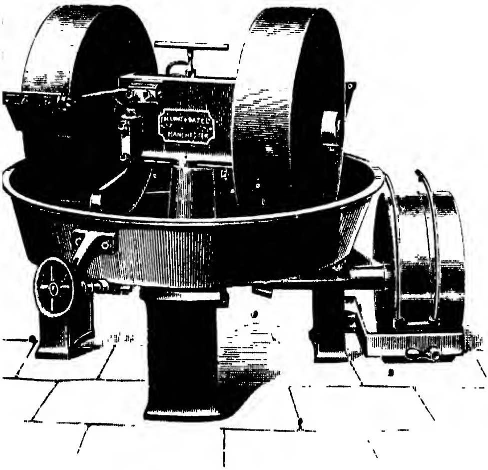


FIG. 14. IRON EDGE-RUNNER MILL. ROTATING-ROLLERS TYPE.

For grinding dry powder.

36. Physical Characteristics of Pigments. The regular pigments differ in appearance by virtue of variation in hue (colour), purity (brightness), opacity (of which the opposite is transparency), and smoothness (fineness and regularity of the particles).

Oil absorption (the amount of oil by weight required to make with the pigment a soft paste) depends upon the shape of the particles,

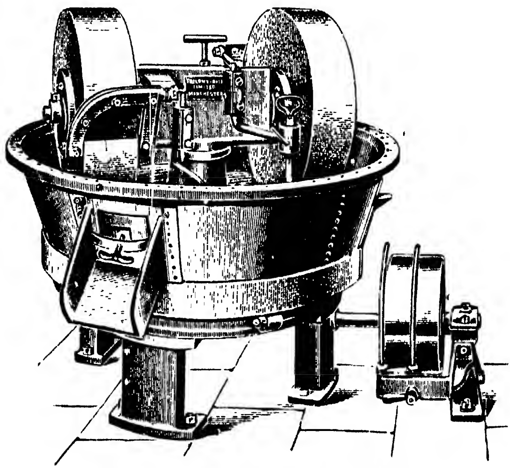


FIG. 15.—GRANITE EDGE-RUNNER MILL ROTATING-ROLLERS TYPE.
For grinding dry powder.

their size, and their specific gravity (*see* Table III, § 33).

Thus china clay (§ 45) with a specific gravity about one-half that of barytes requires not twice the weight of oil that barytes does (per lb. of pigment) but *much* more, owing in part at least, to the finer state of division of the clay.

37. Zinc Oxide. This is an opaque white pigment of very smooth texture, and bulky in powder form. It is manufactured by distilling spelter or zinc ores and allowing air to mix with the hot gaseous metal, whereby a fume of the oxide is produced. Sometimes it is made by precipitating zinc solution by means of sodium carbonate or hydrate and calcining the product.

Its white colour in the best grades is very pure and unrivalled by any other pigment; this is one reason for its use in white enamels (§ 30; for another reason *see* § 31). The best grades are 99·9 per cent pure zinc oxide, the usual and chief impurity being a trace of lead sulphate. Lower grades are priced chiefly according to the purity of the colour. Sometimes the oxide is treated with a trace of ultramarine blue (§ 59) to convert a reddish or yellowish tinge to a greyish one, but although this improves the "whiteness" of the pigment at a superficial glance, yet in reality the shade is darkened by the treatment.

38. Leaded Zincs. When the ore from which zinc oxide is made contains lead (usually as the sulphide galena) the fume produced, when the gasified ore is burnt by admitting air, contains a proportion of lead sulphate or basic lead sulphate which may be as high as 30 per cent. Such "leaded zincs" are often of

very good white colour, of opacity approaching that of the purer zinc oxides and yield very durable paints with linseed oil, which have been found to compare with those made by an admixture of normal zinc oxide and basic carbonate white lead. They are largely made and used in America.

39. Lithopone. This is an opaque white pigment, usually of very good purity of colour. It is composed of barium sulphate and zinc sulphide in intimate association, and is manufactured by precipitating a solution of barium sulphide (from reduction of heavy spar) with zinc sulphate, the mixture reacting to form insoluble barium sulphate and insoluble zinc sulphide. It owes its opacity, which is on a par with that of zinc oxide, to the zinc sulphide content since barium sulphate is transparent in oil. Its opacity is greater than would be expected if the zinc sulphide and barium sulphate were merely present as a mixture and, in explanation of this phenomenon, it has been suggested that each particle of the pigment consists of barium sulphate completely surrounded by zinc sulphide (i.e. adsorbed). Lithopone is usually 30 per cent zinc sulphide, the rest being barium sulphate, these being the proportions mutually precipitated. Lithopones with an excess of barium sulphate are, however, found on the market. Usually lithopone contains

a small proportion of zinc oxide, formed accidentally during the process of manufacture.

Lithopone finds an extensive use in the manufacture of distempers (§ 83) for interior decoration, owing to its great opacity and pure white colour, in conjunction with the fact that it is normally cheaper than zinc oxide and the other white pigments, and is non-poisonous. There is one great drawback to the use of lithopone in distempers, viz., that it is liable to turn grey on exposure to sunlight, more or less regaining its pure white colour after a period of darkness. This is an extraordinary phenomenon not fully understood. There are lithopones on the market for which it is claimed that this defect has been overcome.

Lithopone is not considered a good pigment for use in oil paint, as paints made from it perish sooner than when made from other white pigments. If lithopone is used in conjunction with lead pigments there is a possibility of mutual reaction whereby black lead sulphide would be formed, to the great detriment of the colour. However, this combination of pigments does not always lead to disaster, and is sometimes used.

40. Basic Carbonate White Lead. This has been the principal opaque white pigment in use over a long period, and it is only in recent years that its supremacy has been challenged.

For many years men sought a substitute for white lead owing to the poisonous nature of all the compounds of lead. No material having all the properties of white lead as a pigment has yet been produced, and probably never will be, as the users of paints are at last beginning to realize that it is deficient in some qualities possessed by other white pigments.

The chief advantage of white lead lies in its close texture when ground in oil so that although its opacity *weight for weight* is less than that of others, nevertheless a paint of easy application made from it will often cover better in a coat equally applied than a paint of equal ease of application made from one of the other white pigments, say zinc oxide. Another property that white lead imparts to paint is that of softness of film both when freshly applied (when it is very soft and thus disadvantageous) and when old, when it is not so hard as with some other pigments, and this is a desirable trait.

The disadvantages of basic carbonate white lead are—

(1) Its poisonous nature, causing lead poisoning by inhalation of dust when rubbing down the paint with sand paper, etc., to get a good surface.

(2) The film tends to perish rather more quickly than one containing, say, zinc oxide ("chalking").

(3) It discolours in foul atmospheres by

formation of lead sulphide from the sulphuretted hydrogen in the air.

41. Basic Sulphate of Lead. This pigment is similar to the basic carbonate just described, but is not considered to be quite so poisonous. It is made by direct distillation of galena (*PbS*) in a current of air. It is made largely in America, and is believed to be superior to the basic carbonate in resistance to sulphur fumes and in the lasting qualities of the oil-containing coatings in which it may figure.* Many zinc oxides contain a proportion of this pigment in intimate association (§ 38.)

41 (*a*). **Antimony Oxide and Titanium Oxide.** These are opaque white pigments, which are not yet fully established in the trade. They are both of very high opacity and are inert chemically, and can therefore be mixed with any varnish medium without thickening it unduly, as sometimes occurs with zinc and lead pigments. Antimony oxide, made by a certain English firm under the trade name of "Timonox," is a very good white colour rivalling the best grades of zinc oxide. Titanium oxide is marketed pure but also in a reduced form in which barium sulphate is incorporated just as in the case of lithopone (§ 39).

* Reports of the Scientific Section of the Paint Manufacturers of the U.S.

42. Transparent Fillers. Having now surveyed the range of opaque white pigments, we come to a consideration of the transparent white pigments. Their transparency is not perfect, and varies from one to another, and according to the medium concerned, depending on the smallness of the difference between their refractive index and that of the medium. While being transparent in oil and spirit, these fillers are opaque to a considerable degree in water, and quite opaque when dry. Some of the series show a perceptible degree of opacity even in oil, but they none of them show a pigment strength at all comparable with the series of opaque white pigments if under the same conditions (*see* Table IV).

As they have little or no obliterating power in oil media and are usually cheaper than the opaque white and the coloured pigments, they have been in the past mainly looked upon as adulterants. This is a false view in most cases, as they perform distinct functions. Thus, some of them, such as china clay, terra alba, asbestos, and whiting, are used to prevent the settlement of heavy and dense pigments, and others to produce a certain degree of roughness in a paint to enable subsequent coats to get a firm hold. Their greatest use, however, is to fulfil the chief functions of pigments in a paint, i.e. (1) to enable the oil to be applied to a vertical surface in a thick enough layer for adequate protection which

would not be possible without them, as the oil would run down ; and (2) to form, with the

TABLE IV

REFRACTIVE INDICES, ILLUSTRATING TRANSPARENCY AND OPACITY OF PIGMENTS

SUBSTANCE.	Refractive Index	Difference between Refractive Index of Substance and that of Linseed Oil.	Relative size of Particles	Opacity in Oil
Water	1·33			
Linseed Oil	1·48			
Tung Oil	1·52			
Turpentine	1·54			
Rosin	1·54			
Barytes	1·64	0·16	Relatively large	Practically transparent
Silica	1·54	0·06	,,	Practically transparent
Calcspar	1·65 (1·48)	0·17 to zero	,,	Practically transparent
White Lead	1·8 (2·00)	0·32 to 0·52	Relatively small	Opaque in layers above 1 grm. per 45 sq. cm (approx.).
Zinc Oxide	2·0	0·52	,,	Opaque in layers above 1 grm per 30 sq. cm (approx.).
Zinc Sulphide	2·2	0·72	,,	Renders lithopone, which contains 30% zinc sulphide, as opaque as zinc oxide

oil as the cement, a compact layer of resistant material.

These considerations apply only when the opaque or coloured pigment is so strong in obliterating power that it is not necessary to use sufficient of it to fulfil the other functions

of a pigment; the use of the cheaper filler is then advisable. This is seen especially in brunswick green paints where the pigment usually consists of 80 per cent to 90 per cent barytes, the balance being the prussian blue, lead chromate, etc. Similarly, in many red paints, the red oxide of iron used is such a powerful colour that over 20 per cent to 30 per cent is quite unnecessary. White paints will not cover perfectly in one coat, even when the maximum amount of opaque white pigment is used, but such paints may advantageously be diluted with a proportion of barytes or similar material, because at least two and often more coats are applied to the surface in order to get a thickness of film affording adequate protection; such a diluted paint in two or more coats will obliterate the under surface quite satisfactorily.

There is yet an additional reason in favour of the use of these transparent fillers, and it is that they are quite inert chemically, and so allow the oil which surrounds them to dry normally to ordinary linoxyn, which then shows its full resistance to disintegration.

43. Barytes. Barytes is a crystalline powder obtained by crushing heavy spar, or mineral barium sulphate. Its fineness depends entirely on the degree of crushing and grinding to which it has been subjected, and some samples are rather gritty. It is perhaps the most widely

used of all paint pigments owing to its low cost and its compact character when ground in a medium. Its compact nature gives to paints containing it: (1) Weight—desired because such paints are sold by weight; (2) a good gloss with but little oil since the compact barytes does not absorb much oil; (3) durability of the dry coating, probably owing to the inert character of the barytes and to the fact that it functions solely as a means for supporting the film of oil on the surface during the long drying period and does not interfere chemically with the nature of the linoxyn-containing film (*see* §§ 28, 42).

Barytes is tested for purity of colour by comparison with a standard placed alongside, both piles of pigment being then moistened with white spirit or similar material. The appearance of the dry powder is deceptive because the pigment-strength of barytes is great in the dry state but almost disappears when the material is wetted by a liquid with refractive index approaching its own (*see* § 42). Although the coloured body which causes its discolouration may also be rendered transparent by this means its *colour* is not removed, and so it becomes noticeable.

44. Blanc Fixe. This pigment is barium sulphate precipitated chemically from a salt of barium (usually barium chloride or sulphide) and a soluble sulphate. Chemically it

is the same as barytes, but physically it is quite different. Blanc fixe is an impalpable powder composed of uniform very fine particles, whereas barytes is a very irregular, coarsely crystalline powder as would be expected from its origin. Because of the far greater fineness of blanc fixe it absorbs more oil than barytes, and also possesses a greater opacity (§ 36).

It finds considerable use in place of barytes in enamels (§ 30) where the grittiness of barytes would rule out this substance.

Its power of producing a very good sheen in flat paints or distempers (§ 83) in which it is used is one of its most valuable properties. It should be tested for sulphides which would injure any lead paint with which it might be mixed.

45. China Clay (Kaolin). This material is an almost transparent "pigment" in oil. The chemical composition is silicate of aluminium (hydrated), but this fact is of little importance when kaolin is used as a paint-filler, for it is quite inert chemically. It is not, however, physically inert, for it has an exceptionally high content of very small and even colloidally-sized particles which affect the paint into which it enters, out of all proportion to the amount added. This effect is in the direction of making the paint pasty, causing it to show brush marks (§ 33). Where an excessively high percentage of oil is desired

in a paint this property is useful, as it holds the oil up on a vertical surface when it would otherwise run down. China clay is used sometimes to prevent a heavy pigment from settling, and to give a finer and better textured paste with certain pigments ground as stiff pastes (for subsequent thinning).

46. Silica. This is powdered quartz (silicon dioxide, SiO_2) and is absolutely inert. The particles of silica possess sharp angles and for this reason, if for no other, the material is often introduced into paint so that a fresh coat of paint may adhere well to it. The microscopical rough surface which it presents is called "tooth." Silica may be used instead of barytes (§ 43) as a heavy filler, but is not so good as it absorbs more oil thus yielding a paint less dense in texture, and also more costly per cwt.

47. Asbestine. This is a transparent "pigment" of fibrous nature, the particles being unusually long. It is silicate of magnesium, and is used to assist in holding in suspension more granular and heavier pigments, which it is well able to do owing to the peculiar structure of its particles.

It finds a special use in so-called fireproof paints as the interlacing of its particles causes the paint to remain upon a surface after all organic binding material is destroyed, thus maintaining a non-conducting layer.

48. Whiting (chalk, Paris white, powdered marble). This pigment possesses appreciable opacity in oil and quite satisfactory obliterating power in water, hence its great use in distempers (§ 83).

Since this material is calcium carbonate ($CaCO_3$) it is not inert but is easily decomposed by any acid substance, even by carbon dioxide dissolved in rain water. It is also attacked to a very limited extent by resin and oil acids, when ground into paint. This action is sufficient to cause sometimes a thickening of the paint.

There are several forms of whiting, one being ordinary powdered chalk; another, which is the best as regards density, is made by grinding marble; and a third form is that produced by chemical precipitation - usually as a by-product of some industry such as water-softening, which is carried out by many waterworks.

The whiting must be tested for free lime, because even a small proportion would cause a serious thickening to occur in some types of paint.

49. Terra Alba (Gypsum). Though this material is chemically inert it is quite appreciably soluble in water; moreover it contains two molecules of combined water in its crystals ($CaSO_4 2H_2O$). These facts make its use less than would otherwise be the case. It is produced in two forms; one, the mineral

gypsum powdered, and the other the precipitated form made as a by-product in several chemical processes by the neutralization of sulphuric acid with lime or similarly.

The first kind is coarsely crystalline, the crystals being flaky and soft, and is used in making lime blue (a mixture with ultramarine), as it does not take away from the brilliance of the ultramarine colour owing to its particles being transparent lamellae.

The precipitated product is usually in long rod-like crystals which will interlace in the same way as asbestos (§ 47).

Free lime must be looked for in the precipitated form, and its presence should condemn the sample.

Plaster of Paris is a partially dehydrated gypsum which would have the property of absorbing any moisture in a paint vehicle or other pigments with which it was ground and so might prove useful under certain circumstances.

COLOURED PIGMENTS

50. Drop Black. Bone black, vegetable black, and similar blacks are made from different kinds of organic matter.

Carbon blacks and lamp blacks are made by collecting soot from the burning of natural gas, paraffin oil, tar oils, etc., in an insufficiency of air. These are nearly pure carbon.

Drop black, vegetable black, etc., are made by calcining organic matter and so contain the ash of the said organic matter in addition to the carbon.

The chemical composition of the blacks varies from 100 per cent to 10 per cent of carbon, the rest being inorganic matter, which in the case of the true drop blacks made from bones is principally calcium phosphate.

All the blacks greatly delay the drying (oxidation, § 11) of oils and varnishes with which they are ground, providing the carbon content of the paint exceeds a certain minimum, say, 3 per cent of the oil.

This inhibitive action is as yet unexplained. One theory is that impurities, such as tar oils, retained by the carbonaceous pigment are the cause, as it is a well-known fact that tar oils introduced into a drying oil retard or prevent its drying. On the other hand, carbon pigments which contain only a trace of oil extractable by means of ether, and which have been made by burning oils (such as paraffin) which themselves do not prevent oil from drying, will nevertheless act as powerful inhibitors.

It may be that the carbon acts as an anti-catalyst, or it may adsorb the catalytic metal compounds, removing them from the reacting mixture.

Most of these blacks are of a fine deep colour, especially American carbon black from natural gas and drop black from bones. The inferior

blacks have a tendency to a brownish tone, which may be corrected by admixture with prussian blue (§ 58), and this is also done with the better blacks when a blue-black tone is desired in a paint.

The staining power when mixed with say, white, varies greatly, the pure blacks being very strong stainers indeed, and twenty times as strong as those containing a low percentage of carbon.

51. Graphite. This mineral is a crystalline allotropic modification of carbon, and is not to be confused with the "carbon" blacks. It often contains large proportions of siliceous matter, which is probably an advantage to it, and it may well be that it owes its value not to the intrinsic worth of graphitic carbon but to the inert matter which the pigment contains. A high percentage of graphite, unless diluted ("reduced") with inert materials, has been shown to function badly as a protective pigment. On the other hand, when properly compounded with other pigments, graphite produces a surface on the paint of such a nature as to give some additional protection to the oil film beneath it.

52. Oxides of Iron. There is a large variety of oxides of iron used as pigments. The oxides vary according to whether they come from a mineral source pure and simple, whether

they are prepared by some simple processes from a mineral, or whether they are manufactured as a by-product in some chemical operation. They vary in chemical composition and purity, and very greatly in hue, brilliancy, opacity, oil absorption, etc.

The purest oxides, most brilliant colours and strongest stainers, are obtained from copperas by ignition, in the manufacture of fuming sulphuric acid. The colours obtained vary from a scarlet to a purplish tone, the former being called "Turkey" reds, the latter "Indian" reds. Some mineral oxides yield pigments with colours almost as bright as these, and are also termed "Turkey" and "Indian" according to shade.

Reds are obtained from iron liquors, in many industries, by precipitation with soda and calcining the product. When the iron is in solution as sulphate and is precipitated by lime, the product contains a high percentage of calcium sulphate, and is usually known by the name "Venetian" red. Venetian reds contain about 30 per cent Fe_2O_3, and are of a bright brick red colour.

Very similar in all respects, except that of colour, are the several grades and shades of brown oxides of iron, varying from yellow-browns to purple-browns. Owing to the dullness of shade they are cheaper than the bright red oxides of otherwise corresponding quality. They are mostly of direct mineral

origin, and are much used in making brown and chocolate coloured paints. Their opacity is good, and their staining power fairly good in the purer grades.

The black oxide (Fe_3O_4, magnetic oxide) is also used in paint.

53. Umber. Umber is an earth colour of rather low opacity, containing about 10 per cent of manganese oxides, and of a greyish-brown shade. When ignited and then called "burnt umber" it has a rich and transparent deep yellowish-brown colour. It contains inert material such as clay, and sometimes organic matter. Its oil absorption is very high.

54. Ochre and Sienna. Siennas consist of ferric oxide or hydroxide and inert matter such as clay, and are transparent. They have high oil absorptions. The raw sienna is of a deep golden-yellow colour, and the calcined (burnt) sienna is of a rich brownish-red colour. Ochres are similar in nature, containing a high proportion of clay, etc., but they are dull yellow in colour and fairly opaque. They may contain lead chromate added to brighten them — this should be looked upon as adulteration, although it is a more costly material.

55. Red Lead. This is an oxide of lead (Pb_3O_4) which often contains a proportion of

litharge (PbO), which is possibly the cause of its reaction with acid oils and even with normal linseed oil in which it soon settles and hardens so that such a paint has to be made just before use. Red lead is a bright orange-red colour, and is very heavy and dense yielding a workable paint with a very small proportion of oil. It is much prized as a pigment in priming coats of paint. On iron it may have an inhibitive effect on rusting, owing to its peroxide nature setting up the passive state. It is made by the action of heat and air on litharge (PbO). Another form called orange lead, produced from white lead, is a lighter powder of a brighter yellower colour, and lacks the exceptional protective qualities of ordinary red lead. It does not form such a dense paste with oils and does not settle like the heavier red lead.

56. Yellow Chrome. Lead chromate yellows are brilliant pigments of good opacity varying from a very pale yellow (primrose) through "lemon," "middle," and "orange" chrome to a reddish-coloured pigment "Chinese" red or "Derby" red. The composition varies with the colour, the paler varieties containing sulphate of lead or carbonate, etc., the "middle" chrome being practically pure chromate of lead ($PbCrO_4$) and the deeper colours being basic chromates, containing $PbOPbCrO_4$.

These pigments are permanent to light but are discoloured by sulphuretted hydrogen, as is only to be expected from their composition. The colour of the deeper reddish types is likely to be spoilt by fine grinding as the full depth of colour is caused partly by the large crystalline formation of these pigments.

57. Zinc Chrome. Zinc chromate is a pale yellow pigment of lower tinctorial power than normal lead chromate, and is not so brilliant, reflecting a larger proportion of white light; it corresponds with "primrose" chrome (§ 36) in tint.

It finds a use partly owing to its being comparatively non-poisonous (distempers, § 83) and partly owing to its slight solubility in water rendering it an inhibitor of rust because of its oxidizing nature—chromates are well known inhibitors of rust, inducing the passive state in iron (*see* red lead, § 55).

58. Prussian Blue. Prussian blue is a transparent colour of very great staining power. It varies somewhat in tone, but is usually of a very deep greenish-blue when ground in oil. Its composition is complex, being a ferric ferrocyanide, often with a proportion of sodium or potassium in the molecule. Many varieties are very difficult to grind finely enough to obtain the full staining value from the colour, and so it is often precipitated on to barytes,

and is thus diluted and its full tinting value obtained. It is then called Brunswick blue. These blues are permanent to light and acids, but are easily decomposed by alkalis and so are not used in distemper.

Prussian blue tint in conjunction with white lead is liable to fade temporarily when closed in a package, but regains its original tint after painting out: possibly, this is due to temporary reduction, followed by reoxidation.

59. Ultramarine Blue. Ultramarine blue is a rather transparent but very brilliant colour (a reddish tone of blue), the staining power of which does not approach that of Prussian blue. It is a double silicate of sodium and aluminium containing sulphur, and is an artificial "lapis lazuli." The sulphur is loosely bound as in sulphides, and is easily freed (as sulphuretted hydrogen) by acids, so that ultramarine blue should not be used with lead pigments. The colour, however, is permanent to light and to alkalis and so is very largely used in distemper (§ 83).

60. Brunswick Greens. These greens are composed of varying proportions of Prussian blue (§ 58), lead chromate (§ 56), and barytes (§ 43), according to tone and purity. Owing to their great colour, strength, and brilliancy, they are by far the most largely used greens

in oil paints, and owing to the colour strength of the active ingredients, the percentage of barytes is usually high (up to 90 per cent or higher) and yet such pigments are fully effective when made up into paint. The colour can, of course, be made anything from that of Prussian blue itself (Brunswick blue) through dark bluish-green, middle green, and light yellowish-green to that of lead chromate itself. It is usual to find three grades—dark, mid and light—the actual tones being different for different makers. As a rough guide, the proportions of lead chromate to Prussian blue may be taken as 7 : 3 for dark, 8 : 2 for middle, and 8 : 1 for light.

The colour is found to retain its original hue much longer after application and to possess other advantages if the two coloured constituents are precipitated on the barytes more or less at the same time, and so Brunswick greens although analytically the same as, differ essentially from, a mere mixture of lead chromate, Prussian blue, and barytes.

If mixed as a pale tint with white lead, the same temporary fading may occur as with Prussian blue (§ 58) and so such a tinted paint may show temporarily a much yellower hue, regaining its original colour after painting out.

61. Chrome Oxide Green. This material (Cr_2O_3) is a very permanent green, and is used

for tinting distemper. Its tinting power is considerable, but not so great as that of the Brunswick greens, while it is much more expensive and its tone not so brilliant. The hydrated oxide is more brilliant than the normal oxide.

62. Lakes. Lake colours are made by the precipitation of a dye on to a more or less inert base such as barytes (§ 43), blanc fixe (§ 44), china clay (§ 45), alumina, red lead (§ 56), and orange lead. Thus there are produced after drying, pigments which possess the colours and brilliancy of the dyestuffs used, and are, therefore, brighter than most inorganic or mineral colours, which is the chief reason for their existence. It is found that lake colours are much more used in reds than in greens, for example, because the common mineral reds (iron oxides) are not very brilliant, whereas the common inorganic greens, Brunswick greens (§ 60), and emerald green (copper aceto-arsenite) are very clean and brilliant colours.

Some lakes are as fast to light as are mineral colours, but others fade rapidly in sunlight. Some are quite insoluble in oil and similar mediums, but others are not and are said to "bleed." "Bleeding" is that phenomenon seen when a coating containing a soluble dye is repainted, the colour dissolves in the oil of the new coat, diffuses through it and makes

itself visible at the surface of the new coating, modifying the shade if different from its own.

Some dyes, such as eosins, used for lakes (vermilionettes) are acidic in nature and so may form insoluble salts with metals such as lead and barium; others, such as magenta (maroon lake), are basic, and so may form insoluble bodies in combination with acids such as tannic acid; yet others are of a coarse colloidal nature and deposit easily on to adsorbent surfaces such as that of green earth, which explains why such earthy materials are sometimes found as the basis of lakes, when they are otherwise not desirable for their own sake and do not find an extensive use in the preparation of coatings. Thus greens of basic character (brilliant green) may be precipitated on to green earth, and are used in distemper for tinting.

CHAPTER V

COATINGS WHICH DRY BY EVAPORATION OF SOLVENTS

COATINGS which dry principally by the volatilization of one or more of the ingredients are of widely differing types, and will be treated in this chapter according to the nature of the solvents employed.

TURPENTINE. WHITE SPIRIT. LIGHT NAPHTHAS

63. Resins Used. Coatings using these solvents are made usually with a rosin (§ 79) or rosinate basis: other superior resins are more costly, but have better properties for certain purposes. There may be mentioned here, Kauri, soft Manilla, the various qualities of Damar, and the several copals (§ 15). Kauri requires turpentine (§ 13) as solvent, Manilla can be used with an admixture of alcohol (§ 77) with coal tar naphtha (§ 73) or benzol, while the copals mostly require a preliminary heat treatment and the introduction of some oil to get them into solution (§ 17).

The rosinates used are those of calcium, lead, manganese, magnesium, aluminium, and zinc, the calcium rosinate being by far the

most commonly employed. The object of converting the raw rosin into calcium rosinate is to make a material with a higher softening temperature and hence a less tacky film. This is called "hardening" the rosin. Usually only about one-half the rosin is converted into the calcium rosinate, as a higher degree of combination is difficult to obtain by simple heat treatment.

The rosinates of lead and manganese have been used for the same purposes as that of calcium, and their use follows from their employment as driers (§ 11) for oils and oil varnishes. Thus sometimes they are added to increase the rate of drying of the class of coating under consideration, by false analogy with their action in drying oil vehicles. In the case of coatings which dry by evaporation alone, lead and manganese compounds cannot hasten the rate as they do when acting as catalysers of oils which resinify by oxidation (but see short-oil varnishes, § 66). Lead rosinate may quite logically be used in preference to calcium rosinate, for the sake of its own physical properties, calcium rosinate being less resistant to moisture and, according to some observers, rather easily hydrolysed into free lime and rosin under certain conditions.

64. Softeners. Besides the volatile matter and the rosin, rosinates or other resins, it is usually desirable to introduce a softener of

the resins, for they are very brittle and friable after the volatile material has completely evaporated. Such softeners are mineral oils of any suitable quality, rosin oil, varnish fume (§ 17), non-drying and semi-drying glyceride oils such as tallow, rape oil, cotton seed oil, etc., and drying oils such as raw linseed oil (§ 7), stand oil (§ 9), etc. The latter operate as softeners first as liquid oils, which condition they retain for very long periods owing to the deliberate exclusion of driers, and especially if compounds which inhibit their oxidation are purposely added. Drying oils may also act as softeners in the form of the oxidized product linoxyn, in which case a large proportion of lead rosinate, etc., is usually present to bring about the oxidation. This brings us to that class of composition known as gold size (§ 67), short-oil varnish, terebine (§ 68), etc. When the drying oil is still further increased we arrive at the ordinary type of elastic varnish such as copal varnish which is discussed in Chapter II.

Before passing to a consideration of these largely-used coatings in which the softener is finally an oxidized product, it is necessary to note that soft resins (oleo-resins) are sometimes used in conjunction with the hard and brittle ones to achieve the same object as the simple oil softeners already considered. Guttapercha and india-rubber might also be mentioned in this connection.

65. Manufacture of Quick-Drying Paints, etc. Most of the varnishes and media considered above are easily made by simple mixing in the cold. A cylinder capable of holding the batch, which may be very large is held in a horizontal position, and a shaft runs along the axis carrying knives which are placed radially at intervals. This shaft is made to rotate at a convenient rate and achieves the solution of the resin, etc., in the solvent in a few hours. The charge is admitted through a hole in the top which can be closed by a lid, and a pipe let into the bottom and fitted with a tap suffices to let out the finished mixture.

Pigments are ground in these media in the same cone mills as are suitable for grinding linseed oil paints. Quick-drying paints are thus produced suitable for special purposes where quick drying is essential and where the special weather-resisting qualities and durability of linoxyn are not required.

66. Short-oil Varnish. The remarks in the preceding paragraph do not apply to the mixtures containing linseed oil known as short-oil varnishes, gold sizes, etc. These are always made by processes involving heat, and are very largely used as transparent varnishes as well as for the manufacture of pigment-containing coatings.

Short-oil varnishes and gold sizes dry first by the evaporation of the solvent, and then more fully by the oxidation and resinification of the oil contained therein. The name gold size is applied to some types which are still semi-fluid when the volatile matter has evaporated, and these belong to the type of oil varnish described in Chapter II, although they usually oxidize to a film much more rapidly owing to the very large amount of drier present. There is, in fact, continuous gradation of constitution and properties from a very elastic oil varnish containing much oil at one extreme, to a brittle resinous gold size containing very little oil at the other extreme, and there is no special point at which the dividing line may be drawn. The nomenclature is loose, as is found everwhere in this industry. Generally speaking a short-oil varnish is the same as an elastic copal varnish (long-oil varnish) except for the much smaller proportion of oil, which causes it to present a fairly firm coat by the mere evaporation of the solvent (turpentine or white spirit). Its method of manufacture is the same as that of the more oily varnishes, dealt with in Chapter II.

Short-oil varnishes can be made with a proportion of rosin (§ 79) and are then much inferior in resisting abrasion and atmospheric influences, though their gloss and initial appearance is likely to be improved.

67. Gold Size. Gold sizes are of very differing types, some made with copal (§ 15), some with rosin (§ 79) as basis, but nearly all have a large proportion of metallic drier (§ 11) incorporated. The name follows from the use of such varnishes for sticking gold leaf to surfaces. For this purpose the gold size is applied and then allowed time to become tacky before the gold leaf is spread upon it. By restricting the application of the gold size to the exact portions of the surface which it is desired to coat with gold, the leaf is made to adhere only to such portions and may be trimmed off at the edges.

68. Terebine. "Gold sizes" are now used for a variety of other purposes, the name has lost its original significance, and the varnishes which come under this heading vary greatly. Some are practically short-oil copal varnishes, as previously described, without a very great amount of drier, others largely consist of rosinates (§ 79) of the drying metals, and their principal use is to be mixed with linseed oil to cause it to dry. Such gold sizes when so used are better termed terebines. Terebines are solutions of metallic rosinates, linoleates, oleates, etc., in white spirit or turpentine, and are used solely as a convenient means of introducing the metal catalyst into drying-oil and mixtures or varnishes which contain drying oil. They are usually made of

a lower viscosity than gold sizes in order to facilitate their amalgamation with the oil or to deter the user from adding too great a quantity. This thinness, however, is not necessary or even desirable. Should too great a quantity of terebine, containing rosinate, be added to a paint or varnish it may be bad for the durability of the film. The metals present as driers are lead, manganese, and (or) cobalt (§ 11).

Here again we find a looseness of nomenclature and a gradation of characters without any definite dividing line between varnishes, gold-sizes, and terebines.

69. Uses of Gold Size. The original use of gold size and one for which it is still required is for the application of gold leaf and other metallic leaves as described in § 67; or for giving a similar effect by dusting on metallic powder. Other common uses are:

(*a*) Mixture with paints containing linseed oil, to cause the oil to dry and to give a harder coat. For this purpose, the gold size must be of that sort which contains much rosinate or linoleate of lead, etc.

(*b*) Making quick- and hard-drying paints for coach builders' use (§ 5), as undercoats. These paints dry flat in appearance and admit of rubbing down. In this instance the high class gold size, containing the best copals and no rosin, is best; and the copal used and the

method of manufacture must be such that the gold size will not feed, i.e. thicken unduly; with basic lead carbonate or with zinc oxide.

(*c*) As a medium for metallic powders, like aluminium powder, which require a medium which will hold the powder tenaciously even before the drying oil (if such is used in the mixture) has had time to oxidize, especially as the metallic powder sometimes will exclude air and greatly delay the oxidation. In this case also a high class gold size is desirable, which will not react with the metal of the powder, dulling its appearance and causing it to clot together. The free acid should be kept very low, if necessary by addition of lime during the manufacture of the gold size.

(*d*) As a varnish where quick-drying is very desirable but durability not important, as in cheap stains for domestic use (§ 2) when a bright varnish finish and a stain is required in one application.

70. Substitutes for Linseed Oil. Certain types of the class of coating considered in this chapter happen to be much cheaper to produce than those containing linseed oil and the various modifications thereof, and so we find types which are made to imitate linseed oil paints in their rate of drying—the rate of evaporation being prolonged purposely to simulate the behaviour of oils which dry by

oxidation. Such mixtures are used as substitutes for linseed oil, and are made up into paints which behave more or less like true linseed oil paints in application, smell, appearance, etc., but which have not the protective quality of the genuine article, since the resin which remains when all the very slow volatilizing ingredient has gone, has not the durability of the oxidized product left from the oxidation of drying oils. Moreover, the percentage of resin left is only about 60 per cent of the "oil" (the rest being volatile) whereas the proportion of oxidized product of linseed oil left in the paint film is actually more than the oil originally introduced. This distinction is shown clearly by Table V. The durability of a paint is largely dependent upon the ratio of binder remaining in the dried film and the superiority of linseed oil paint in this respect, apart from the greater durability of linoxyn compared with resin, is shown by the Table.

The resin for such substitute paints is often common rosin with or without the addition of metallic rosinates, such as those of lead and manganese, which are sometimes added for mere camouflage—colour and analysis. There is, as a corporate part of the resinous residue, a non-volatile non-drying oil such as mineral oil (as is used for lubricating),* the presence of

* *See* also ***Lubrication and Lubricants***, **by J. H. Hyde. Uniform with this volume. (Pitman, 2s. 6d. net.)**

which prevents the resin from becoming too friable and brittle. Rosin alone quickly becomes so friable that on rubbing gently it will dust away as though it were a powder already; the oils added cannot altogether prevent this tendency of the rosin. Other softening oils

TABLE V

COMPARISON BETWEEN LINSEED OIL PAINT AND RESIN SUBSTITUTE PAINT

	Both Paints when Wet.*	When Dry. Linseed Oil Paint.	When Dry. Substitute Paint.
Parts, by weight—			
"Oil"	30	35	20
Pigment	65	65	65
Turpentine added to get easy working under brush	5	—	—
Ratio, Oil : Pigment	6 : 13 or 46%	7 : 13 or 54%	4 : 13 or 31%

* The substitute paint is compounded to imitate the linseed oil paint when wet.

which may be added are rosin oil, varnish fumes (§ 17), varnish foots, oil foots—in fact any non-volatile oil which will form a homogeneous mixture with rosin.

From the foregoing it must not be thought that such linseed oil substitutes are without

any protective value. If carefully proportioned and made up into paint they will produce coatings of quite unexpected durability, especially for inside use. Their appearance is satisfactory at first, but there is a tendency to poor gloss owing to the low proportion of residual oil and resin, and to the development of surface cracks and markings.

The volatile matter used is white spirit (§ 14) of low quality, i.e. having a long "tail"—a large proportion of difficultly volatile matter as shown by the distillation test. This grade is used, because it is cheap and owing to the presence of additional difficultly volatile matter which is desirable in this instance; the low quality is thus no detriment. The difficultly volatile portion may be the petroleum distillate lying between white spirit and lubricating oil, sometimes called gas oil, or other similar product, also the non-volatile and the difficultly volatile may be added as one single ingredient. Some types of varnish fume (§ 17) are partially volatile, partially non-volatile oil, and partially resin or the residue becomes resinous on exposure to the air. It is not possible in such substitute oils to decide where the volatile ends and the difficultly volatile begins; where the difficultly volatile ends and the non-volatile oil begins; and where the non-volatile oil ends and the resin begins. The blendings possible to attain the desired effect are legion.

Points to be taken into consideration in addition to those outlined already are—

(1) The oil must be capable of being used with either lead carbonate (§ 40) or zinc oxide (§ 37), without combining with either to form a solid, or too stiff a paste.

(2) Paint made with the oil must be able to contain a large proportion of barytes (§ 43) without settling down hard. This is necessary as these paints must be cheap and barytes is an ingredient which greatly conduces to this end.

(3) Generally speaking, the maximum durability of a substitute paint is obtained when the "non-volatile" oil is of such a nature that it volatilizes, resinizes, or otherwise disappears as slowly as possible, thus continuing to function—for it must be remembered that the term non-volatile oil may be only relative, and that in time resins originally containing heavy oils will be found to have become brittle. On the same score, this ingredient should be present in a proportion as high as possible without causing other faults such as stickiness and undue softness.

(4) If high gloss is required the proportion of non-volatile oil in the mixture must be low and the resin high as the glossy surface must be hard enough to withstand touching with the finger without marking—such "enamels" are made and dry quickly with a very good appearance, but they are very brittle and are useless out of doors.

BITUMINOUS COATINGS

71. Black Bitumen Coatings. There are two fairly distinct varieties of black coatings which owe their blackness to the type of resin used and not to added dry pigment, as in the case of black paints proper. In one group, coal tar pitch, and coal tar oils are employed; and in the other, the principal constituents are bitumens originating in the refining of petroleum or of a direct mineral origin. Coatings in the first group do not lend themselves easily to admixture with ingredients not of a coal tar origin, though such other ingredients can be and are sometimes added in small proportions. Moreover, these coatings do not admit of the addition of drying oils, for the coal tar compounds inhibit the formation of linoxyn, etc. The coal tar pitch is not easy to get into satisfactory solution, and it is easily thrown out again at small provocation, such as by injudicious additions to the varnish. This class is used principally as cheap black coatings for exposed ironwork for which purpose they have proved very satisfactory (§ 4).

72. Coatings with Petroleum Base. These coatings do allow of the addition of drying oils, for the bitumens of petroleum origin do not interfere markedly with the drying of linseed oil. They may also be used in conjunction with copals (§ 15) and will dissolve in volatile

solvents of coal tar extraction and also in many others, such as white spirit, turpentine, rosin spirit. These bitumens lend themselves to a considerable variety of purposes. Some are compounded to compete with the coal tar type of coating for protection of ironwork in exposed situations and where under the destructive influences of acids, water containing electrolytes, etc. Other recipes are designed to yield coatings with a very high gloss and fine appearance, but without much strength or lasting qualities, known as Brunswick blacks which find a use in the home, to give a bright black finish of a more or less temporary nature to domestic utensils, stoves, etc. These blacks may contain rosin (§ 79) to give gloss, and bone pitch to give a deep black. The mineral bitumens or asphalts of the highest quality, such as gilsonite, form part of many black enamels, containing much drying oil, which first dry by the evaporation of the white spirit or turpentine contained and then harden by the oxidation of the linseed oil or other drying oil. Black enamels such as these usually contain added black pigment since the proportion of dark-coloured asphaltum is not sufficient to give the required opacity.

73. Coatings with Coal Tar Base. In these coatings coal tar pitch is the base and coal tar naphthas are the volatile solvents. The pitches from coal tar vary greatly among themselves, according to the method by which the coal has

been carbonized, and (though not so much as might be expected) according to the source of the coal from which the tar has been distilled. Coal tars are distilled and yield benzole, the coal tar naphthas of graduated boiling points, naphthalene, anthracene, anthracene oils, and pitch. The pitch from horizontal- and inclined-retort tar usually contains a high percentage of free carbon, about 50 per cent, which gives to it a pasty consistency after it has been softened by heat, and this same pasty effect is seen in the black varnishes made from it. In view of this free carbon pigment, such black coatings should properly be called paints. The pitch from vertical-retort tar contains a much smaller percentage of free carbon, about 25 per cent, so varnishes made from it flow more freely than those from the inclined-retort coal tar pitch. Pitch of similar character to these is obtained from water-gas tar, but its content of carbon is very low, and it is likely to partake more largely of the nature of petroleum asphaltum, especially when coming from carburetted water-gas.

By combining the various pitches with tar, anthracene oil (green oil), and the various coal tar naphthas a great number of recipes can be prepared, without going outside the products of coal tar. Coatings of this type differ rather widely in their ease of working, rate of drying, appearance when fresh and

appearance when old, and in their protective value. The protective quality is usually high in spite of the cheap source of the ingredients, and is higher than that of many coatings costing much more.

These varnishes are incompatible with oil paints and varnishes, and if used over fresh oil paint will soften or even dissolve it. One or two coats of the bituminous solution alone should be applied.

ALCOHOLIC VARNISHES

74. Shellac. The principal resin of those which yield varnishes with alcohol is shellac. This is the product of an insect which lives in India, and coats with resin the twigs of the trees on which it swarms.

Shellac is a very valuable material owing to its extremely tough nature; it is hard enough to resist much abrasive action, and is not very brittle. It forms a film, left after the evaporation of an alcoholic varnish, which will entirely resist the thumb nail. Shellac comes into the market in several forms, most of which contain a small percentage of rosin (§ 79), which is said to be added to facilitate the refining process, making the shellac melt more easily, but which is also added as an adulterant since the cost of shellac is so high and that of rosin so low.

Crude shellac is deeply coloured red with the lac dye which is another product of the same insect and various expedients are used to

decrease or eliminate this colour. Garnet lac usually contains rosin, is deeply coloured, and is sold in thick pieces (also moulded and then called button lac). Standard T. N. Shellac usually contains not more than 3 per cent rosin, and is of a pale orange colour; it is sold in rather thin flakes. Lemon Shellac is similar but much lighter in colour.

Bleached Shellac is quite colourless, the last traces of dye having been destroyed in a process of bleaching with chlorine, which incidentally considerably modifies the nature of the shellac itself. This bleached product contains water (the process necessitates precipitation from an aqueous solution) and it is a strange fact, that the lac is only soluble in alcohol so long as it is still in this moist condition, for if it is dried or kept too long it becomes insoluble in alcohol or indeed in any solvents, and will only swell therein. Carelessly made qualities show a tendency to softness and stickiness, especially when the varnish film is warmed.

There are many other less definite grades of lac on the market.

Tests. Since shellac is liable to adulteration with rosin it is important to know if this is present and if so, the proportion. The quantity of rosin is estimated from the iodine value of the resin since that of rosin is very high (about 230) while that of shellac is very low (about 18).

Shellac is easily dissolved in alcohols, ethyl alcohol (i.e. methylated spirit) or methyl alcohol (i.e. wood spirit) in any plant which provides sufficient agitation, which is so designed that the alcohol will not be allowed to evaporate rapidly, and in which there is no danger of fire or sparking. A horizontal cylindrical mixer is suitable.

75. Usefulness of Shellac. The proportion of shellac required to make a varnish of convenient consistency for brushing is about 35 per cent, which is much lower than that of most other resins in alcohol or white spirit, naphtha, etc. The coating yielded by a shellac varnish is therefore thinner than that yielded by most of the others, nevertheless its resistance to scratching, rubbing, etc., is much higher than that of the others. The shellac film, however, is not very resistant to atmospheric influences, and will slowly absorb moisture, turning white. This latter effect is less likely to be found where the shellac has been baked on, or is very old. Thus a shellac film is not suitable as a protective coating out of doors, but is very satisfactory for articles which are much handled indoors, as its film is absolutely non-tacky.

Most of the lacquers found on metal articles are of shellac baked on—the articles having been coated with the shellac solution while warm and dried in a warm, moisture-free

atmosphere, and then baked for a short time at a low heat.

The shellac film is insoluble in most of the ordinary organic solvents and so shellac varnish finds an application as a medium for paints resisting petrol, benzol and naphtha ; for which purpose, pigments, the same as those used with linseed oil media, are ground into the shellac varnish, or metal powders such as aluminium powder are mixed in, where such a metallic effect is required.

76. French Polish. Most articles of furniture (§ 5) are coated with a thick, firm, glossy crust of resin, which should be pure shellac, that has been applied in the special manner known as French polishing.

In this process of application a thin shellac solution in alcohol (about 1 to 10) is rubbed over the wooden surface by means of a pad of cotton wool wrapped in a small piece of soft non-fluffing fabric. The soddened pad is passed quickly over the whole area of the article to be coated touching each part once only—then when this very thin coat has hardened, which takes place quickly, the pad is again swiftly and dexterously passed over the surface. This is repeated many dozens or even hundreds of times until a good thickness of resin results. It is necessary to moisten the pad with raw linseed oil (§ 7), to allow it to slip over the surface satisfactorily, but very

little must be used. The resin layer is rubbed down with pumice as many times as is necessary to get an even grainless surface. The final polishing which yields the splendid finish of French polish calls for great skill and is completed with clean pads, very slightly moistened with alcohol, which are first rubbed very lightly and then more heavily over the surface, continually adding traces of alcohol to the pad until all oil is removed from the resin surface.

77. Soft Manilla. Manilla varnishes are largely used where shellac (§ 76) would be too expensive, or where greater gloss is required than shellac would afford, when applied by brush. Manilla varnish takes the place of French polish in cheaper articles of furniture, bannisters, rails, etc. (§ 5). It will allow of handling without showing tackiness, and has a fine appearance. It has, however, the same defect as shellac, in turning white by absorption of moisture and it is therefore useless for outdoor application. It is not suitable for mixing with any but the inert pigments, as the acids of this varnish are very reactive, thickening up with basic pigments and corroding metallic powders. Manilla varnish is paler in colour than shellac varnishes, excepting varnish made from bleached shellac.

78. Sandarac. This resin is pale and dissolves easily in methylated spirit. Its uses

are much the same as those of manilla and shellac. It is rather weak and brittle, and is used for mixing with shellac in brush varnishes or polishes as they are called, to cheapen the product and to give more gloss and a clearer and thicker film.

79. Rosin. Rosin or colophony is used in alcohol varnishes for cheapness, and to give gloss, but it always greatly reduces the strength of the resultant coating. It is not used alone, as it is equally soluble in cheaper solvents than alcohol, and of course these would be used in preference, if ever a simple rosin solution were wanted.

Rosin is a highly acid, extremely brittle resin obtained as a residue when turpentine is distilled off from the oleo-resins of pines. The metallic salts are known as rosinates. Its combining weight may be taken to be about 350. It is very largely used in conjunction with linseed oil, etc., for making varnishes, and in quick-drying coatings using white spirit as solvent (*see* § 63).

CELLULOSE VARNISHES

80. Nitro-Cellulose. Collodion and celluloid require a proportion of ketonic or ester solvents in the mixture which is to bring them into solution, and even then only a comparatively small proportion can be dissolved, if a solution not too viscous for brush application

or dipping is to be obtained. A 10 per cent solution in the case of collodion or celluloid (estimated on collodion content) is about the maximum for brushing—5 per cent makes a quite fluid solution, and will actually yield a better coating than the 10 per cent solution owing to the latter dragging and pulling up after the brush, leaving streaks and patches almost uncovered. The above percentages are only intended to be suggestive, since the viscosity varies greatly with the particular mixture of solvents used, and these figures will apply to the better mixtures of solvents rather than to the inferior.

Collodion is nitro-cellulose, and is made by the action of concentrated nitric and sulphuric acids on cotton or other kinds of pure cellulose. The forms containing fewer nitro groups are usually called collodion, and those containing more are called guncotton and used as explosives.*

Celluloid is made from all types of nitro-cellulose, and is nitro-cellulose with which has been incorporated a proportion of a compound to reduce its explosive or inflammable nature. The safety ingredients may be added in solution, in which case collodion is first dissolved and the collodion solution thus transformed into a celluloid solution; or they may be

* See also *The Manufacture and Uses of Explosives*, by R. C. Farmer. Uniform with this volume. (Pitman, 2s. 6d. net.)

incorporated by mastication with but a small proportion of solvent. The compounds used for this purpose are very diverse.

Camphor is commonly used but, not unexpectedly, has the objectionable feature of imparting its odour to the celluloid. Camphor is the product obtained from the *Laurus Camphora* of Japan. It can be made chemically from turpentine, but the natural camphor is the commercial article. Some other compounds used for the same purpose as camphor are castor oil, naphthalene, triphenyl phosphate and cellulose acetate.

Suggested recipes for cellulose nitrate varnishes are given in Table VI.

TABLE VI

VARIOUS RECIPES FOR CELLULOSE NITRATE VARNISHES

	Parts by Weight.				
	(a)	(b)	(c)	(d)	(e)
Cellulose Nitrates	5	5	5	5	5
Acetone	—	—	—	35	—
Amyl Alcohol	—	—	30	—	—
Amyl Acetate, or Ethyl Acetate	—	95	35	20	35
Methyl or Ethyl Alcohol	50	—	—	20	30
Ether	45	—	—	20	—
Benzol	—	—	30	—	30
Camphor, etc.		As required.			

Solvents for Cellulose Nitrate Varnishes. Amyl acetate (pear oil) is a powerful solvent and

may be used alone. Its low volatility makes any varnish, containing a good deal of it, dry slowly and evenly, but its odour is very strong and characteristic.

Amyl alcohol (or mixed alcohols, fusel oil) can replace the acetate to some extent, and operates in the same way in making the varnish more tractable; its odour is also objectionable.

Ethyl acetate is similar to amyl acetate, but not so effective, as it is more volatile and not such a good solvent. On the other hand, its odour is less powerful.

Ethyl alcohol or methyl alcohol, or the mixture methylated spirit, will not dissolve celluloid, nor will ether; but the two together, ether and alcohol, will dissolve celluloid. Ether or alcohol may be used as diluent after the celluloid has been dissolved in amyl acetate.

Ether thins out a solution more easily than any of the other solvents, and this is its function when added, but this result may easily be rendered ineffective owing to the very rapid evaporation of the ether during application.* Moreover, this rapid evaporation causes cold and thus leads to deposition of moisture on the drying varnish, with a great risk of spoiling the film, or making it opaque. Other solvents which can be used in moderate proportion are turpentine, white spirit, acetone oils, chlorhydrin, acetic acid.

* Ether boils at 35° C. (95° F.).

81. Uses of Cellulose Nitrate Varnishes. These varnishes are used for coating articles which are to be much handled, as the film obtained is very tough, not easily scratched, and not softened by grease or moisture. They are also used for a large variety of minor purposes, such as-

(1) Lacquering metals with a colourless solution which hardly changes the appearance of the metal.

(2) Colouring glass, metals, etc. In this case a suitable dye (soluble in the solvents used, i.e. spirit soluble) is added to give the desired effect. Small electric bulbs are dipped in such solutions for decorative effects or to produce photographic ruby lights.

(3) Impregnating gas mantles to hold together the very delicate threads, of oxides of cerium and thorium, during transit and handling.

(4) As a coating for small wounds and cuts to keep dirt out and allow quick healing.

(5) As a dope for aeroplane wings—though the other cellulose ester, cellulose acetate, is much more largely used for this purpose.

(6) As a medium for powdered metals such as aluminium powder—though the low proportion of cellulose nitrate that can be got into solution does not enable it to bind a large percentage of the powder satisfactorily.

Nitro-cellulose varnishes are not easily applied with a brush unless only the slowly

evaporating solvents are present and, as a thick layer of liquid varnish is desirable in order to obtain an appreciable thickness of the dry cellulose nitrate film, it is usual to coat objects by dipping or by pouring the varnish over the object and allowing it to drain.

82. Cellulose Acetate. Varnishes of which this is the solid ingredient are made using mixed ketonic alcoholic and ester solvents. Their principal use, and one for which they are considered pre-eminent, is as coatings for aeroplane wings (" dope "). They possess the valuable property of shrinking the fabric, so making it taut to an unusual degree.

DISTEMPERS

83. Simple Distemper. A distemper in its simplest form consists of glue (size), water and whiting (§ 48), which is sometimes called " whitewash," and is often tinted bluish with ultramarine blue (§ 59).

It can easily be seen that using whiting (which is very cheap) as the chief pigment in high proportion, water as the volatile matter and glue as the binder, a very cheap coating is obtained with much to recommend it on the score of appearance. It will cover up ugly or dirty surfaces more effectively than will oil paint; it is very easily applied with large brushes owing to the low viscosity of the medium; and, under such conditions, it can

be applied quite thinly and rapidly, and therefore cheaply. This, in conjunction with the very cheap ingredients, makes it possible to cover large surfaces at very low cost. Moreover, these considerations make it possible to recoat at fairly frequent intervals, and so cleanliness and good appearance may continually be maintained. Distempers are especially suitable for use on rather absorbent surfaces.

The defects of distempers are as obvious as the advantages. The coating is not impervious to water, and so has low protective value. Where much water is present it will become soft and may wash off. Where the atmosphere is damp the size will putrify (unless much preservative has been incorporated) and then the whiting, having lost its binder, will easily rub off or even dust and flake off of its own accord. This is often seen in dwellings. especially in the sculleries where intermittent dampness favours the disintegration.

Distempers of this simple type are sold cheaply, usually in powder form, to save the cost of a watertight package and the additional transport charges. In these cases the glue is in the form of a fine powder intimately mixed with the pigment and thus rapidly swells and goes more or less into solution when the powder distemper is mixed even with cold water. The powder is mixed and ground in edge runner mills, *see* Figs. 13-15, pp. 54-56.

84. Casein. Casein may be substituted for glue in powder distempers in which case a little alkali is present as casein is not soluble otherwise. When casein is used the resulting coating cannot easily be washed off, but it is more friable and liable to rub off or be easily scratched off when dry. The resistance of the film to water, when once it has been thoroughly dried, is due to the insolubility of casein in water. When mixing the distemper, the casein is got into solution by the aid of an alkali, such as hydrate of calcium (slaked lime). After the coating is applied, the alkali is neutralized gradually by the carbon dioxide of the air, being converted into chalk (calcium carbonate) which has not the power to assist the casein into aqueous solution. Such a distemper would allow of a certain amount of sponging and washing down, and might be termed a washable distemper (§ 85).

85. Washable Distemper. More elaborate distempers are made containing additional ingredients to improve the properties in several directions.

For instance, washable distempers and sanitary distempers are pastes of glue, water, linseed oil or copal varnish, preservative and disinfectant, with a high percentage of whiting (§ 48), lithopone (§ 39) or other pigments ground in.

Since they contain oils, etc., these distempers

are sold in paste form only. The paste is usually soft enough to allow of its being mixed cold and by hand, with the requisite amount of cold or luke-warm water to thin it to a suitable consistency for use. From some points of view it is desirable that the proportion of glue should be low; for instance, so that the paste is not very gelatinous, but owes its modicum of rigidity partly to the high percentage of pigment, thus allowing it to be mixed with water cold If the glue were in sufficient proportion fully to gelatinize the mass then water could not be mixed in to thin it until it had been made fluid by heating. With such a distemper it is necessary to place the keg in a pail of hot water before thinning, and to use hot water for thinning.

The linseed oil (§ 7), etc., has the effect of increasing the resistance of the film to water, and operates also as an additional binding agent. As the water evaporates out of the glue, the oil which has hitherto been present in an emulsified form, oozes out on to the surface of the glue film and partly protects it from moisture. It might be expected that the oil in drying would harden the glue by the aldehydes evolved, but the evidence is against this.

However, in spite of such palliatives and in spite of the name "washable distemper," such paste distempers as described will rarely stand more than gentle sponging.

The disinfectants used are of more importance than might at first appear. Their first function is to preserve the paste, and their second is to prevent putrefactive decomposition of the glue, etc., after application to the surface. In addition, they disinfect the walls to which the distemper is applied. Without a proper proportion of suitable disinfectant, the distemper would be better termed "insanitary" rather than "sanitary" distemper.

The manufacture of distemper is carried out in the same way as that of oil paint, the medium being, of course, a watery one. The medium is first made up completely, including the emulsification of the oil, and the pigment is then ground in it. As an example of a water paint recipe the following will serve—

	Per cent by weight
Glue	5
Linseed Oil	5
Water	35
Lithopone	55

Disinfectant and stainer are added to the mixture as required and, for cheapness, the lithopone may partially be replaced by whiting.

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Treatise on Colour Manufacture, by Zerr, Rubencamp & Mayer. (Griffin.)

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Many other volumes are in preparation for the series of Technical Primers, full particulars of which can be obtained from the publishers at Pitman House, Parker Street, Kingsway, W.C.2.

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